Aspects of the Inorganic Chemistry of Rubber Vulcanisation. Part 4.[1] Dialkyl- and Diaryl-dithiophosphate and -dithiophosphinate Complexes of Zinc: Phosphorus-31 Nuclear Magnetic Resonance Spectral Studies and Structures of $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ and $[NEt_4][Zn(S_2PPh_2)_3]$ †

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The complexes $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ and $[NEt_4][Zn(S_2PPh_2)_3]$ have been prepared by treatment of $[Zn(S_2PR_2)_2]$ with $[NR'_4][S_2PR_2]$ ($R = OC_6H_4Me\text{-}p$ or Ph, R' = Me or Et). Preparation of $[ZnI_2\{S_2P(OPr^i)_2\}]^-$ and $[Zn(S_2PR_2)_2(S_2CNMe_2)]^-$ ($R = OC_6H_4Me\text{-}p$ or Ph) is also described. From reactions of $[Zn\{S_2P(OR)_2\}_2]$ ($R = Pr^i$ or $C_6H_4Me\text{-}p$) with H_2O_2 or $Bu^tO(OH)$, zinc phosphates and $ZnSO_4$ have been obtained, and $[Zn\{S_2P(OPh)_2\}_2]$ and $[Zn\{S_2P(OPh)_2\}_3]^-$ react with ROH ($R = Et$ or Pr^i) in solution to give amongst other products $[Zn\{S_2P(OR)_2\}_2]$ and $[S_2P(OR)_2]^-$ with loss of phenol. The ^{31}P n.m.r. spectra of a series of dialkyl- and diaryl-dithiophosphate and -phosphinate complexes have been recorded and used to establish rapid exchange within the equilibrium $[Zn\{S_2P(OR)_2\}_3]^- \rightleftharpoons [Zn\{S_2P(OR)_2\}_2] + [S_2P(OR)_2]^-$. The structures of the title compounds have been determined crystallographically: $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ is monoclinic with $a = 29.311(9)$, $b = 11.032(3)$, $c = 17.515(5)$ Å, $\beta = 106.83(2)°$, space group $P2_1/a$, $Z = 4$, and 2 490 reflections give R 0.0532; $[NEt_4][Zn(S_2PPh_2)_3]$ is monoclinic with $a = 11.160(6)$, $b = 9.962(5)$, $c = 43.11(3)$ Å, $\beta = 104.73(5)°$, space group $P2_1/c$, $Z = 4$, and 3 304 reflections give R 0.0411. Both have slightly distorted tetrahedral geometries in which one S_2PR_2 ligand is bidentate, and the other two are unidentate.

In previous papers of this series[2,3] we have described the possible significance of anionic zinc thiolato-species in the ZnO–thiuram disulphide or 2-mercaptobenzothiazole–stearic acid accelerated vulcanisation of ' diene ' rubbers. We have reported on the syntheses and structural characterisations of the salts of $[Zn(S_2CNMe_2)_3]^-$, $[Zn(C_7H_4NS_2)_3(H_2O)]^-$, and related Cd^{II} species,[1] including $[Cd\{S_2P(OPr^i)_2\}_3]^-$.

An important objective of our work is the understanding of how these compounds behave in *solution*, since we believe that the vulcanisation process could occur in a homogeneous phase in the rubber matrix which might act, in effect, as hydrocarbon solvent. However, an inherent difficulty in pursuing this goal is the lack of suitable ' spectroscopic handles ' in these zinc complexes. It seemed probable that zinc dialkyl- and diaryl-dithiophosphate $[S_2P(OR)_2]$ and -phosphinate $[S_2PR_2]$ species might have a chemistry similar to that of their dithiocarbamato- and benzothiazole-2-thiolato-analogues. If this view was correct, then the main advantage of developing this chemistry would lie in the study of the ^{31}P n.m.r. spectra of the complexes prepared. Such studies of thiophosphate and related species had already been made by Glidewell,[4] indicating the feasibility of our approach. However, it was most important to establish to what extent zinc dithiophosphate and phosphinate chemistry actually paralleled that of the related dithiocarbamato- and benzothiazole-2-thiolato-systems. In particular, we needed to know whether ZnO reacted with the simple dithiophosphato-species $HSP(S)(OR)_2$, $[^-S(S)P(OR)_2]_2$, or $[S_2P(OR)_2]^-$, and whether anionic complexes of the type $[Zn\{S_2P(OR)_2\}_3]^-$ or $[Zn(S_2PR_2)_3]^-$ could be formed and were stable. If these anionic complexes could be prepared, then we would be in a position to establish their behaviour in solution using ^{31}P n.m.r. spectroscopy. Some preliminary studies have been reported.[5]

Results and Discussion

Synthetic Studies.—In a typical vulcanisation system, zinc oxide, certain specific organosulphur compounds *e.g.* thiuram disulphides $(^-S_2CNR_2)_2$ and benzothiazole-2-sulphenamides $C_7H_4NS_2\text{–}NR_2$ (R = alkyl), S_8, and stearic acid are allowed to react at *ca.* 140 °C to form the ' sulphurating agent.' This is, in effect, activation of S_8 prior to attack on the rubber hydrocarbon. We have shown[2,3] that ZnO reacts with $(^-S_2CNR_2)_2$ or $C_7H_4NS_2\text{–}NR_2$ (R = alkyl) to give $[Zn(S_2CNR_2)_2]$ or $[\{Zn(C_7H_4NS_2)_2\}_n]$, and that these complexes react further with stearate anion (as a quaternary ammonium salt) to give $[Zn(S_2CNR_2)_3]^-$ and $[Zn(C_7H_4NS_2)_3(H_2O)]^-$.

In refluxing xylene, in the presence or absence of S_8, zinc oxide did *not* react with $[^-S_2P(OPr^i)_2]_2$. Even when $NH_2(C_6H_{11})$ was added to a mixture of ZnO and $[^-S_2P(OPr^i)_2]_2$ (amines are occasionally added to vulcanising systems, usually in the form of a sulphenamide), the oxide was recovered virtually quantitatively, although some $[NH_3(C_6H_{11})][S_2P(OPr^i)_2]$ was formed. There was no reaction between ZnO and either $[NMe_4][S_2P(OPr^i)_2]$ or $[NH_2(C_6H_{11})_2][S_2P(OPr^i)_2]$ in refluxing toluene, and when stearic acid was added to the latter reaction system, using xylene as the reaction medium, zinc stearate and $[NH_2(C_6H_{11})_2][S_2P(OPr^i)_2]$ were recovered. There was no evidence for the formation of $[Zn\{S_2P(OPr^i)_2\}_2]$ in any of the foregoing reactions.

However, when ZnO was treated with $HSP(S)(OPr^i)_2$ in refluxing propan-2-ol, $[Zn\{S_2P(OPr^i)_2\}_2]$ was obtained in good

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† Tetramethylammonium bis(*OO'*-di-*p*-tolyl dithiophosphato-*S*)-(*OO'*-di-*p*-tolyl dithiophosphato-*SS'*)zincate and tetraethylammonium bis(diphenyldithiophosphinato-*S*) (diphenyldithiophosphinato-*SS'*)zincate.

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Supplementary data available (No. SUP 23508, 68 pp.): structure factors, thermal parameters, least-squares planes, H-atom positions, bond distances and angles, ^1H n.m.r. data of selected dithiophosphato- and dithiophosphinato-complexes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical data (%)

Compound	Calc.				Found			
	C	H	N	S	C	H	N	S
$[NMe_4][S_2P(OMe)_2]$	31.2	7.8	6.1	27.7	31.4	7.9	6.0	27.7
$[NMe_4][S_2P(OEt)_2]$	37.1	8.6	5.4	*a*	37.0	8.5	5.4	*a*
$[NMe_4][S_2P(OPr^i)_2]$	41.8	9.1	4.9	*a*	41.2	9.1	4.9	*a*
$[NBu^n{}_4][S_2P(OPr^i)_2]$	58.0	11.1	3.1	14.1	58.1	11.2	2.8	14.7
$[NMe_4][S_2P(OPh)_2]$	54.1	6.2	3.9	18.0	54.5	6.5	4.0	20.7
$[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$	56.4	6.8	3.7	16.7	56.3	6.7	3.7	16.7
$[NMe_4][S_2PPh_2]$	59.4	6.9	4.3	19.8	60.7	6.6	4.5	21.4
$[C_5H_5NH][S_2PPh_2]$	62.0	4.9	4.3	19.5	62.2	4.9	4.2	19.6
$[Zn\{S_2P(OPr^i)_2\}_2]$ [b]	29.3	5.7	*a*	26.1	28.9	5.5	*a*	26.9
$[Zn(S_2PPh_2)_2]$	51.7	3.6	*a*	23.0	52.3	3.7	*a*	23.3
$[Zn(S_2PEt_2)_2]$	25.8	5.4	*a*	34.5	26.3	5.5	*a*	34.9
$[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}]$	48.9	4.1	*a*	18.7	48.7	3.8	*a*	18.9
$[NBu^n{}_4][ZnI_2\{S_2P(OPr^i)_2\}]$ [c]	34.1	6.5	1.8	8.3	34.5	6.7	1.7	8.1
$[NEt_4][ZnI_2(S_2PPh_2)]$ [d]	34.4	4.3	2.0	9.2	35.0	4.6	2.0	9.0
$[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$	51.8	5.1	1.3	18.0	51.2	5.3	1.3	18.3
$[NEt_4][Zn(S_2PPh_2)_3]$	56.0	5.3	1.5	20.4	56.2	5.6	1.6	20.4
$[NEt_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(S_2CNMe_2)]\cdot 2H_2O$	48.3	5.6	2.9	19.8	48.1	5.4	3.2	22.5
$[NMe_4][Zn(S_2PPh_2)_2(S_2CNMe_2)]$	49.1	5.1	3.7	25.4	49.2	5.5	3.8	25.9

[a] Not determined. [b] Obtained by two different routes, see Experimental section. [c] Iodine analyses: Calc. 32.8, found 32.5%. [d] Iodine analyses: Calc. 36.3, found 36.3%.

yield, and this compound could also be obtained using $[NH_4][S_2P(OPr^i)_2]$. In this last reaction, ammonia must be evolved, but we found no evidence for $[Zn(NH_3)_2\{S_2P(OPr^i)_2\}_2]$. This is not surprising since the bis(ammoniate), synthesised independently by addition of ammonia to $[Zn\{S_2P(OPr^i)_2\}_2]$, is thermally labile, readily losing NH_3 to regenerate the bis(dithiophosphate) complex. Pyridine also forms a bis adduct, but dicyclohexylamine afforded only $[NH_2(C_6H_{11})_2][S_2P(OPr^i)_2]$ when it reacted with $[Zn\{S_2P(OPr^i)_2\}_2]$. The diphenyldithiophosphinato-complex $[Zn(NC_5H_5)(S_2PPh_2)_2]$, which is analogous to $[Zn(NC_5H_5)(S_2CNMe_2)_2]$,[6] was obtained by reaction of $[C_5H_5NH][S_2PPh_2]$ with zinc acetate.

We have shown that ZnI_2 reacted with one mol equivalent of $[NR'_4][S_2CNR_2]$ forming 1 : 1 adducts $[NR'_4][ZnI_2(S_2CNR_2)]$.[2] The dithiophosphato- and dithiophosphinato-anions behaved similarly, and we have obtained $[NBu^n{}_4][ZnI_2\{S_2P(OPr^i)_2\}]$ and $[NEt_4][ZnI_2(S_2PPh_2)]$ (analytical and ^1H n.m.r. spectral data; Table 1. ^1H N.m.r. spectra for all the complexes described herein are consistent with the formulation of the compounds, and are otherwise unremarkable). We were unable to prepare $[NBu^n{}_4][ZnCl_2\{S_2P(OPr^i)_2\}]$ by the same route, obtaining instead $[NBu^n{}_4][ZnCl_4]$.

Attempts to prepare $[Zn\{S_2P(OR)_2\}_3]^-$ (R = Me, Et, or Pr^i) or $[NEt_4][Zn(S_2PEt_2)_3]$ by treatment of $[Zn\{S_2P(OR)_2\}_2]$ with $[NR'_4][S_2P(OR)_2]$ (R′ = Me, Et, or Bu^n) or $[Zn(S_2PEt_2)_2]$ with $[NEt_4][S_2PEt_2]$ afforded only colourless oils. However, we were able to synthesise crystalline $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ and $[NEt_4][Zn(S_2PPh_2)_3]$.

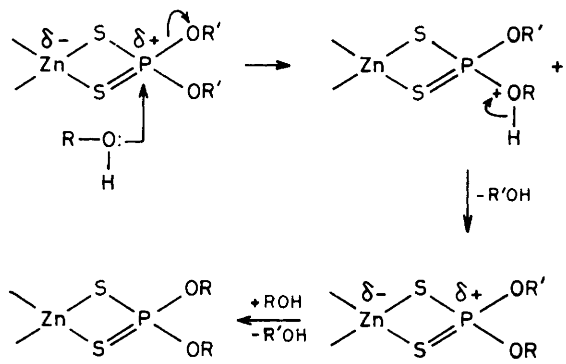
It is known that $[Zn(S_2CNR_2)_2]$ and $[\{Zn(C_7H_4NS_2)_2\}_n]$ react with tetra-alkylammonium stearate giving $[NR'_4][Zn(S_2CNR_2)_3]$ and $[NR'_4][Zn(C_7H_4NS_2)_3(H_2O)]$, respectively.[2] Treatment of 1 mol of $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ with 2 mol of $[NMe_4][OCOC_{17}H_{35}]$ caused an immediate precipitation of zinc stearate, and $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ crystallised slowly from the mother-liquor. However, when the mol ratio of the reagents was adjusted to 1 : 1, again zinc stearate precipitated immediately, but on its removal by filtration, crystals of $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ began to form. From this reaction mixture $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ was also obtained. In our previous study of the reactions of $[Zn(S_2CNR_2)_2]$ with $[NR'_4][OCOR'']$ (R″ = Me, Et, Pr^n, Bu^n, C_5H_{11}, C_9H_{19}, or $C_{17}H_{35}$) we had observed [2] that 1 : 1 carboxylate adducts were formed with R″ = Me, Et, Pr^n, and Bu^n, but with R″ = Bu^n and higher fatty acid salts, $[Zn(S_2CNR_2)_3]^-$ was formed. A comparable investigation of the behaviour of $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ in propan-2-ol revealed that only the tris(dithiophosphato)zincate ion was produced, behaviour similar to that observed with $[\{Zn(C_7H_4NS_2)_2\}_n]$.

We have described the formation of mixed-ligand species $[Zn(S_2CNR_2)_n(C_7H_4NS_2)_{3-n}]^-$ (*n* = 1 or 2) by addition of $[S_2CNR_2]^-$ or $[C_7H_4NS_2]^-$ to the appropriate zinc bis(ligand) complex.[3] Reaction of $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ and $[Zn(S_2PPh_2)_2]$ with the appropriate salts of $[S_2CNMe_2]^-$ did indeed afford $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(S_2CNMe_2)]$ (isolated as the dihydrate) and $[NEt_4][Zn(S_2PPh_2)_2(S_2CNMe_2)]$. However, attempts to prepare mixed-ligand complexes using $[NMe_4][C_7H_4NS_2]$ afforded only $[\{Zn(C_7H_4NS_2)_2\}_n]$ and $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$. Attempts to isolate salts of $[Zn\{S_2P(OR)_2\}_2\{S_2P(OR')_2\}]^-$ were unsuccessful, oils being invariably produced.

Peroxides and hydroperoxides are common reagents in the oxidative degradation of rubbers. It is known that zinc dithiocarbamates and benzothiazole-2-thiolates deactivate hydroperoxides forming oxidised products, *e.g.* possibly $[Zn\{SOC(S)NR_2\}_2]$ or $[Zn\{SO_2C(S)NR_2\}_2]$.[7] Accordingly, we investigated the behaviour of dithiophosphato-species with H_2O_2 or $Bu^tO(OH)$ in water giving, not surprisingly, $[{}^-S_2P(OR)_2]_2$. Treatment of $[Zn\{S_2P(OR)_2\}_2]$ (R = Pr^i or $C_6H_4Me\text{-}p$) with aqueous H_2O_2 in diethyl ether also gave $[{}^-S_2P(OR)_2]_2$ but, in addition, an insoluble zinc compound which did not contain C, H, or S (microanalysis: P not determined). However, i.r. spectral studies revealed a strong band at 1 120 cm^{-1}, suggesting the presence of P=O, so it is possible that the compound is a zinc phosphate. When $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ was treated with two mol of $Bu^tO(OH)$ in diethyl ether, in the absence of water, a white diethyl ether-insoluble precipitate was obtained which could be recrystallised from acetone. Microanalyses of this solid for C, H, and S were not wholly definitive but could be consistent with the empirical formula $C_{42}H_{43}O_7P_3S_6Zn_2$, or $[Zn_2\{S_2P(OC_6H_4Me\text{-}p)_2\}_3(OH)]$. The i.r. spectrum of this compound is very similar to that of $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ but has additional strong bands at 1 200 and 675 cm^{-1}. We have discounted the possibility that the compound is $[Zn\{SOP(=S)(OC_6H_4Me\text{-}p)_2\}_2]$ (having an S=O group) or $[Zn\{OSP(=S)(OC_6H_4Me\text{-}p)_2\}_2]$ analogous to $[Cr\{OSC(=S)NR_2\}(S_2CNR_2)_2]$ (R = Me or Et)[8] (microanalytical data give a fair fit for this formulation) since S=O stretching frequencies for S- and O-bonded Me_2SO complexes occur in the region 1 090—1 120 and 1 025—985 cm^{-1}, respectively, substantially different to that observed in the 'oxidised' dithiophosphate species. However, in the absence of any other useful information, we can draw no definite conclusion. When $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ was treated with four mol equivalents of $Bu^tO(OH)$ in the absence of water, $[^-S_2P(OC_6H_4Me\text{-}p)_2]_2$ and $ZnSO_4$ were isolated, indicating that oxygenation of the sulphur can occur.

During our studies of the solution behaviour of the dithiophosphato-complexes described in this paper, we became aware of the ease with which aryl substituents could be displaced by alkyl groups. Thus, when a small amount of ethanol was added to a hot solution containing freshly prepared $HSP(S)(OPh)_2$ in toluene, effervescence occurred and, on cooling, followed by addition of aqueous $[NMe_4][OH]$ $[NMe_4][S_2P(OEt)_2]$ and *not* $[NMe_4][S_2P(OPh)_2]$ was isolated in good yield. Similarly, when $[Zn\{S_2P(OPh)_2\}_2]$ was treated with $[NMe_4][S_2P(OPh)_2]$ in propan-2-ol, needle-shaped crystals, presumably of $[NMe_4][Zn\{S_2P(OPh)_2\}_3]$ formed initially, but redissolved. After 4 weeks, rhombic crystals of $[Zn\{S_2P(OPr^i)_2\}_2]$ were obtained from the solution. It was subsequently established that when $[Zn\{S_2P(OPh)_2\}_2]$ was allowed to stand in ethanol or propan-2-ol for 4 weeks, exchange took place giving $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i), and the smell of phenol could be detected in the reaction mixture. However, $[NR'_4][S_2P(OPh)_2]$ was quite stable under these conditions. Furthermore, we observed that $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ could be recrystallised from propan-2-ol, and $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ only underwent partial exchange in ethanol over 4 weeks. It is known that the transition-metal compounds $[M\{S_2P(OPh)_2\}_n]$ ($n = 2$, M = Ni or Co; $n = 3$, M = Cr or Rh) undergo this kind of substitution[9] when heated with aliphatic alcohols, but similar behaviour with zinc complexes does not appear to have been previously reported.

The foregoing observations can be interpreted in terms of Lewis-acid-assisted nucleophilic displacement at the phosphorus atom of OR′ by OR (see Scheme). The apparently slow rate of exchange of the *p*-tolyl derivative relative to its phenyl analogue, and the failure of $[NR'_4][S_2P(OPh)_2]$ to undergo any exchange, may be understood in terms of either the electron-releasing effect of the methyl group in $S_2P(OC_6H_4Me\text{-}p)_2$ relative to H in $S_2P(OPh)_2$, or the negative charge on the anion. In each case, the P atom will carry more charge relative to that in $S_2P(OPh)_2$, thus inhibiting nucleophilic attack by ROH.



Scheme. R = alkyl, R′ = aryl.

Table 2. Phosphorus-31 n.m.r. spectral data for dithiophosphato- and dithiophosphinato-compounds

Compound	$\delta(^{31}P)$ [a]	Solvent
$[NMe_4][S_2P(OMe)_2]$	118.9	$(CD_3)_2CO$
$[NMe_4][S_2P(OEt)_2]$	114.1	$(CD_3)_2CO$
$[NMe_4][S_2P(OPr^i)_2]$	113.2	$(CD_3)_2CO$
$[NH_3(C_6H_{11})][S_2P(OPr^i)_2]$	107.0	CD_2Cl_2
$[NH_2(C_6H_{11})_2][S_2P(OPr^i)_2]$	108.4	CD_2Cl_2
$[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$	108.8	$(CD_3)_2CO$
$[Zn\{S_2P(OMe)_2\}_2]$	104.1	$CDCl_3$
$[Zn\{S_2P(OEt)_2\}_2]$	98.6	$CDCl_3$
$[Zn\{S_2P(OPr^i)_2\}_2]$	94.5	$CDCl_3$
	94.2	CD_2Cl_2
$[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$	96.5	$CDCl_3$
$[Zn\{S_2P(OMe)_2\}_2]$ + $[NMe_4][S_2P(OMe)_2]$ (1 : 1)	108.2	$CDCl_3$
$[Zn\{S_2P(OEt)_2\}_2]$ + $[NMe_4][S_2P(OEt)_2]$ (1 : 1)	104.5	$CDCl_3$
$[Zn\{S_2P(OPr^i)_2\}_2]$ + $[NMe_4][S_2P(OPr^i)_2]$ (1 : 1)	100.3	$CDCl_3$
$[Zn\{S_2P(OPr^i)_2\}_2]$ + $[NH_3(C_6H_{11})][S_2P(OPr^i)_2]$ (1 : 1)	98.1	CD_2Cl_2
$[Zn\{S_2P(OPr^i)_2\}_2]$ + $[NH_2(C_6H_{11})_2][S_2P(OPr^i)_2]$ (1 : 1)	97.8	CD_2Cl_2
$[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ + $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ (1 : 1)	100.6	CD_2Cl_2
	101.8 [b]	CD_2Cl_2
$[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ [c]	100.3	CD_2Cl_2
$[NBu^n{}_4][ZnI_2\{S_2P(OPr^i)_2\}]$	94.7	$(CD_3)_2CO$
$[NEt_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(S_2CNMe_2)]$	101.4	$(CD_3)_2CO$
$[NMe_4][S_2PEt_2]$	73.3	$CDCl_3$
$[Zn(S_2PEt_2)_2]$	80.7	$CDCl_3$
$[C_5H_5NH][S_2PPh_2]$	61.3	$CDCl_3$
$[Zn(S_2PPh_2)_2]$	62.8	$CDCl_3$
$[NEt_4][Zn(S_2PPh_2)_3]$	61.6	$CDCl_3$

[a] In p.p.m., relative to 85% H_3PO_4, measured with accuracy of ±0.1 p.p.m., but taking into account solvent and concentration effects, δ is ±1 p.p.m. [b] At −90 °C. [c] Solution made from isolated tris(dithiophosphato)zincate ion.

We also noted that $HSP(S)(OPh)_2$, $[^-S_2P(OPh)_2]_2$, and mixtures of $[Zn\{S_2P(OPr^i)_2\}_2]$ and $[NMe_4][S_2P(OR)_2]$ (R = Ph or $C_6H_4Me\text{-}p$) were unstable in hot or cold acetone, decomposition affording some sulphur, unidentified thiol, and phenol. We were unable to identify the products, but observed that $[NMe_4][S_2P(OR')_2]$ (R′ = aryl) was stable under comparable conditions.

Phosphorus-31 *N.M.R. Spectral Studies*.—Glidewell[4] has shown that the chemical shift of the P atom in $S_2P(OR)_2$ is sensitive to the nature of, and to the group attached to, the S atoms of the dithiophosphato-group. Thus $\delta(^{31}P)$ for ionic species, $[S_2P(OR)_2]^-$, is significantly different, and generally to lower field, of that found for neutral covalent metal-containing species, $[M\{S_2P(OR)_2\}_n]$.

In Table 2 are given the ^{31}P chemical shifts of $[S_2P(OR)_2]^-$ (as quaternary ammonium salts), $[Zn\{S_2P(OR)_2\}_2]$, 1 : 1 mixtures in solution of $[S_2P(OR)_2]^-$ with $[Zn\{S_2P(OR)_2\}_2]$, some authentic anionic zinc dithiophosphato-complexes, and related dithiophosphinato-species. Broadly, the data are consistent with Glidewell's observations. Taking into account some variation of $\delta(^{31}P)$ with changes in solvent and concentration effects, it may be seen that the anionic ligands have chemical shifts in the range 108—119 p.p.m. (relative to external H_3PO_4), the actual position of the signal being in-

Table 3. Variation of $\delta(^{31}P)$ with ratio $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$:$[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$

Ratio	$\delta(^{31}P)$ [a]/p.p.m.
1 : 1 [b]	100.3
1 : 1	100.6
1 : 2	98.4
1 : 3	97.6
0 : 1	96.5
2 : 1	101.2
3 : 1	103.7
1 : 0	108.8 [c]

[a] In CD_2Cl_2, relative to 85% H_3PO_4, ±1 p.p.m. [b] Solution made up from isolated $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$. [c] In $(CD_3)_2CO$ solution.

fluenced partly by the substituent R. The range of $\delta(^{31}P)$ for $[Zn\{S_2P(OR)_2\}_2]$ is 94—104 p.p.m., whereas that for the 1 : 1 mixtures of $[S_2P(OR)_2]^-$ and $[Zn\{S_2P(OR)_2\}_2]$, *where only one signal is detected*, is 98—108 p.p.m., significantly to lower field of the neutral zinc species alone. It must also be noted that $\delta(^{31}P)$ for authentic $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ and the 1 : 1 mixture of $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ and $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ are identical (within the experimental error).

These data strongly suggest that $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ dissociates rapidly in solution, and it seems probable that the equilibrium shown below is established in which

$$[Zn\{S_2P(OR)_3\}_3]^- \rightleftharpoons [Zn\{S_2P(OR)_2\}_3] + [S_2P(OR)_2]^-$$

the $S_2P(OR)_2$ group undergoes fast exchange between the three environments. If this is correct, then addition of an excess of $[S_2P(OR)_2]^-$ to a solution containing $[Zn\{S_2P(OR)_2\}_3]^-$ should *not* result in the appearance of two ^{31}P resonances, but the observed single ^{31}P signal should move towards the position of the signal due to ' free ' $[S_2P(OR)_2]^-$. This is, in fact, observed, and in Table 3 can be seen the effect on $\delta(^{31}P)$ of variations on the relative concentrations of $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ and $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ mixed in solution. Even when solutions of a 1 : 1 mixture of the simple anion and neutral zinc bis(ligand) complex are cooled to −90 °C, only a single resonance was observed, but attempts to add further $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ at this temperature failed because the salt precipitated. Thus, we have established that a fast exchange process, within the equilibrium described above, is established in dichloromethane. Single ^{31}P resonances were also detected in solutions of $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ in chloroform and acetone.

Molecular Structures of $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ *and* $[NEt_4][Zn(S_2PPh_2)_3]$.—The structures of the two anions are illustrated in Figures 1 and 2, in each case with the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are compared in Table 6.

The two anions exhibit almost identical, distorted tetrahedral zinc co-ordination polyhedra comprising a bidentate $[S_2PR_2]^-$ ligand with somewhat longer zinc–sulphur bonds than those to each of the two unidentate similar ligands. The two remaining zinc–sulphur contacts are much longer than those found in the $[Zn(S_2CNMe_2)_3]^-$ anion where a similar distorted tetrahedral co-ordination geometry is found.[3] In a related cadmium species, $[Cd\{S_2P(OPr^i)_2\}_3]^-$, a more regular, but still significantly asymmetric six-co-ordinate geometry is seen,[1] suggesting that zinc cannot accommodate six sulphur atoms in its co-ordination sphere and that the greater distance of the non-bonded sulphur atoms in the present molecules is simply a consequence of the greater bond lengths in a $[S_2PR_2]^-$ group as compared to as $[S_2CNR_2]^-$ group.

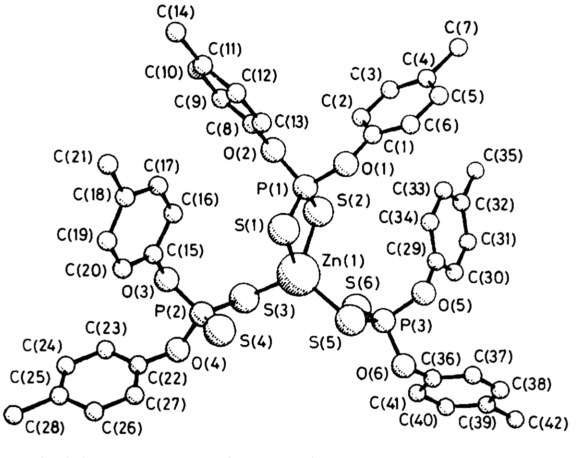


Figure 1. The structure of the anion $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]^-$ with atom labelling

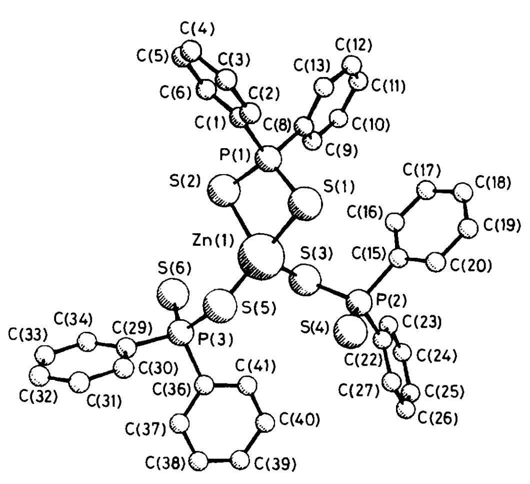


Figure 2. The structure of the anion $[Zn(S_2PPh_2)_3]^-$ with atom labelling

The phosphorus–sulphur bonds to the non-co-ordinating sulphurs are expectedly shorter than other such bonds; the geometries around the phosphorus atoms are essentially tetrahedral. In the $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]^-$ anion, the bond angles at the oxygen atoms are large at 125.7 ± 3.5° and all organic substituents point outwards from the metal centre; the change from *p*-tolyloxy to phenyl seems to have no noticeable effect on the overall structure of the anion except that in $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]^-$ the Zn–S and S–P bond lengths are greater by approximately 0.04 Å ($\sim 8\sigma$). The relationship of the $[Zn(S_2PPh_2)_3]^-$ anion to its cobalt-containing analogue has been previously discussed.[5]

Conclusion

We have shown that the chemistry of zinc dialkyl- and diaryldithiophosphates and -phosphinates is broadly similar to that of their dithiocarbamato- and benzothiazole-2-thiolato-analogues. There are certain small differences in detail, the most significant being structural. However, the variations in geometries between $[Zn(S_2CNMe_2)_3]^-$, $[Zn(C_7H_4NS_2)_3(H_2O)]^-$, $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]^-$, and $[Zn(S_2PPh_2)_3]^-$ can

Table 4. Atomic positional parameters with estimated standard deviations in parentheses for $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zn(1)	0.374 12(5)	0.238 07(15)	0.010 36(9)	C(19)	0.345 1(5)	0.406 0(16)	−0.367 5(9)
S(1)	0.422 28(12)	0.371 9(3)	−0.044 31(21)	C(20)	0.318 0(5)	0.339 3(14)	−0.333 4(8)
S(2)	0.445 45(12)	0.115 3(3)	0.055 07(22)	C(21)	0.424 3(7)	0.475 6(19)	−0.377 9(11)
S(3)	0.318 75(14)	0.114 7(4)	−0.075 30(24)	C(22)	0.208 4(4)	0.197 2(12)	−0.277 2(7)
S(4)	0.292 57(13)	0.396 4(3)	−0.149 17(22)	C(23)	0.204 5(5)	0.116 4(14)	−0.335 9(9)
S(5)	0.351 97(14)	0.352 1(3)	0.103 41(23)	C(24)	0.174 4(6)	0.139 6(16)	−0.409 2(10)
S(6)	0.350 81(14)	0.060 6(3)	0.161 21(23)	C(25)	0.149 2(5)	0.247 6(16)	−0.425 2(5)
P(1)	0.470 76(12)	0.248 5(3)	0.005 23(20)	C(26)	0.153 7(6)	0.327 9(14)	−0.365 6(11)
P(2)	0.290 90(12)	0.224 4(3)	−0.166 88(21)	C(27)	0.182 8(5)	0.301 9(14)	−0.290 1(9)
P(3)	0.357 90(12)	0.229 9(3)	0.189 07(22)	C(28)	0.116 2(9)	0.284 5(21)	−0.506 5(13)
O(1)	0.513 9(3)	0.320 8(7)	0.067 6(5)	C(29)	0.443 1(4)	0.173 8(11)	0.291 9(7)
O(2)	0.495 0(3)	0.191 5(7)	−0.056 1(5)	C(30)	0.437 2(5)	0.096 8(13)	0.347 6(8)
O(3)	0.312 4(3)	0.187 3(8)	−0.236 4(5)	C(31)	0.474 2(5)	0.015 1(14)	0.385 0(9)
O(4)	0.238 4(3)	0.167 1(8)	−0.201 4(5)	C(32)	0.515 1(5)	0.019 3(15)	0.362 0(9)
O(5)	0.406 4(3)	0.259 5(8)	0.257 0(5)	C(33)	0.521 4(5)	0.100 4(19)	0.306 0(10)
O(6)	0.319 8(3)	0.281 8(8)	0.229 8(5)	C(34)	0.483 9(5)	0.181 0(17)	0.270 8(9)
C(1)	0.554 5(4)	0.269 6(10)	0.121 0(7)	C(35)	0.555 3(7)	−0.068 1(20)	0.398 8(13)
C(2)	0.567 1(4)	0.149 7(12)	0.118 2(8)	C(36)	0.313 9(4)	0.233 3(12)	0.299 5(7)
C(3)	0.608 2(4)	0.105 0(12)	0.173 7(8)	C(37)	0.337 0(5)	0.283 3(14)	0.370 1(8)
C(4)	0.636 6(5)	0.179 7(12)	0.230 6(8)	C(38)	0.329 7(6)	0.238 0(17)	0.437 9(8)
C(5)	0.623 3(4)	0.302 0(13)	0.231 9(8)	C(39)	0.300 9(6)	0.138 0(15)	0.438 7(9)
C(6)	0.582 1(5)	0.347 4(11)	0.177 3(8)	C(40)	0.278 5(6)	0.091 9(15)	0.366 0(10)
C(7)	0.681 4(5)	0.133 6(16)	0.290 0(10)	C(41)	0.284 7(5)	0.134 2(14)	0.295 8(9)
C(8)	0.515 2(4)	0.248 5(12)	−0.107 7(6)	C(42)	0.292 8(7)	0.087 7(21)	0.511 9(10)
C(9)	0.527 3(4)	0.179 7(12)	−0.161 9(7)	N(1)	−0.311 8(3)	0.267 4(11)	0.009 0(6)
C(10)	0.547 6(5)	0.224 9(13)	−0.215 1(7)	C(43)	−0.293 1(8)	0.246 1(21)	0.095 9(6)
C(11)	0.556 1(4)	0.352 1(13)	−0.217 9(7)	C(44)	−0.293 3(9)	0.384 2(16)	−0.011 3(13)
C(12)	0.543 8(4)	0.422 2(12)	−0.162 1(7)	C(45)	−0.296 3(9)	0.168 0(18)	−0.034 4(12)
C(13)	0.523 6(4)	0.375 4(12)	−0.106 4(8)	C(46)	−0.364 5(3)	0.271 5(26)	−0.014 1(13)
C(14)	0.578 1(6)	0.408 8(15)	−0.275 0(9)	N(2)	−0.324 7(10)	0.267(3)	−0.004(2)
C(15)	0.338 3(4)	0.259 7(13)	−0.271 6(7)	C(47)	−0.344 1(18)	0.368(4)	0.033(3)
C(16)	0.387 4(4)	0.252 4(14)	−0.243 7(7)	C(48)	−0.356 1(16)	0.160(4)	−0.012(3)
C(17)	0.414 0(5)	0.321 4(14)	−0.279 0(8)	C(49)	−0.322 0(18)	0.305(5)	−0.084(2)
C(18)	0.394 2(5)	0.402 6(14)	−0.340 8(8)	C(50)	−0.276 3(12)	0.236(5)	0.047(3)

Atoms N(1), C(43)—C(46) and N(2), C(47)—C(50) comprise the two components of the disordered tetramethylammonium cation: their estimated standard deviations are derived from those of the group parameters which were used to refine their positions and orientations.

be readily understood in terms of the relative ' bite ' of the respective ligands, and the difficulties in accommodating six large donor atoms at the metal atom.

Our most important observation is that, in solution, the tris(dithiophosphato)zincate ion exists in an equilibrium with $[Zn\{S_2P(OR)_2\}_2]$ and ' free ' anion $[S_2P(OR)_2]^-$. It would seem highly likely that $[Zn(S_2CNR_2)_3]^-$ and $[Zn(C_7H_4NS_2)_3(H_2O)]^-$ will behave similarly in a wide range of solvents, and indeed this has been established electrochemically for $[Zn(S_2CNMe_2)_3]^-$ in acetone.[10]

We believe that the presence of ' free ' sulphur ligand in systems where anionic tris(ligand)zincate species can be generated is highly significant for the activation of S_8 in vulcanisation systems, and this will be discussed in a subsequent paper.

Experimental

Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrophotometers. The ^1H n.m.r. spectra were obtained using JEOL PFT-90 and Perkin-Elmer R-34 instruments. Phosphorus-31 n.m.r. spectra were obtained using a JEOL PFT-90 instrument, at 40.48 MHz in 10-mm diameter tubes. Elemental analyses were determined by the Microanalytical Laboratory of this Department.

Preparations and Reactions.—$[NR'_4][S_2P(OR)_2]$ (R′ = Me, Et, *or* Bu^n; R = Me, Et, Pr^i, Ph, *or* C_6H_4Me-*p*). To a solution of $HS_2P(OR)_2$ (0.1 mol) in toluene (50 cm^3) was added an aqueous solution of $[NR'_4][OH]$ (0.1 mol). The mixture was stirred overnight, the aqueous layer extracted with diethyl ether (2 × 20 cm^3), and the toluene and diethyl ether combined. The organic solvent mixture was then evaporated *in vacuo* affording a solid residue which was washed with toluene and ligroin (b.p. 30—40 °C). The compound was obtained as white crystals upon crystallisation from acetone (yields 70—90%).

$[C_5H_5NH][S_2PPh_2]$. To a solution of HS_2PPh_2 (12.5 g) in methanol was added pyridine (4.0 g) at a slow rate and with stirring. The compound formed slowly on standing, was collected by filtration, and washed with diethyl ether (yield 14.8 g, 90%).

$[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$. To a suspension of P_4S_{10} (11.1 g) in toluene (60 cm^3) was added a solution of *p*-MeC_6H_4OH (22 g) in toluene (10 cm^3). The mixture was then refluxed until a clear solution had formed, when the solvent was evaporated *in vacuo* affording $HS_2P(OC_6H_4Me\text{-}p)_2$ (yields 80—90%).

To a solution of $HS_2P(OC_6H_4Me\text{-}p)_2$ (31.0 g) in toluene (60 cm^3) at room temperature was added an aqueous solution of $ZnSO_4 \cdot 7H_2O$ (14.4 g). The mixture was stirred vigorously overnight, the organic layer was then separated, washed with water (2 × 30 cm^3), and evaporated *in vacuo*. The resulting oil was dissolved in diethyl ether–ligroin (b.p. 30—40 °C) mixtures (1 : 1 v/v) and the solution allowed to stand for 24 h during which time the compound formed as white microcrystals. These were collected by filtration and washed with ligroin (b.p. 30—40 °C) (yield 27.3 g, 80%).

Reaction of ZnO *with* $HS_2P(OPr^i)_2$. To a suspension of ZnO

Table 5. Atomic positional parameters with estimated standard deviations in parentheses for $[NEt_4][Zn(S_2PPh_2)_3]$

Atom	*X/a*	*Y/b*	*Z/c*
Zn(1)	0.393 35(8)	0.174 35(9)	0.119 68(2)
S(1)	0.229 95(17)	0.024 92(21)	0.089 90(4)
S(2)	0.485 03(17)	0.136 72(21)	0.074 38(4)
S(3)	0.316 58(17)	0.390 24(20)	0.115 06(4)
S(4)	0.164 90(21)	0.227 76(24)	0.163 57(5)
S(5)	0.491 21(17)	0.077 97(20)	0.168 14(4)
S(6)	0.686 70(19)	0.292 58(20)	0.146 43(4)
P(1)	0.328 62(17)	0.033 31(20)	0.057 04(4)
P(2)	0.158 36(17)	0.362 32(21)	0.130 28(4)
P(3)	0.639 88(17)	0.201 61(20)	0.181 94(4)
C(1)	0.364 1(7)	−0.133 9(7)	0.045 29(15)
C(2)	0.308 6(8)	−0.245 2(8)	0.054 38(18)
C(3)	0.338 1(9)	−0.372 1(9)	0.046 06(20)
C(4)	0.425 5(8)	−0.389 5(9)	0.028 76(20)
C(5)	0.480 3(8)	−0.279 4(9)	0.019 46(21)
C(6)	0.451 0(7)	−0.153 4(9)	0.028 02(18)
C(8)	0.238 3(6)	0.108 5(7)	0.020 59(16)
C(9)	0.243 1(7)	0.244 9(9)	0.016 09(17)
C(10)	0.173 4(8)	0.305 1(10)	−0.011 13(20)
C(11)	0.094 2(8)	0.229 5(11)	−0.034 46(20)
C(12)	0.088 1(9)	0.094 8(11)	−0.030 16(19)
C(13)	0.160 6(8)	0.031 2(9)	−0.002 97(18)
C(15)	0.031 8(6)	0.332 1(7)	0.095 02(16)
C(16)	0.038 8(7)	0.361 6(9)	0.064 32(17)
C(17)	−0.062 0(7)	0.337 2(10)	0.038 62(18)
C(18)	−0.169 9(7)	0.287 5(9)	0.043 15(20)
C(19)	−0.177 5(7)	0.258 2(9)	0.073 82(20)
C(20)	−0.077 9(7)	0.279 4(9)	0.100 3(18)
C(22)	0.125 9(6)	0.530 6(7)	0.143 19(16)
C(23)	0.121 5(7)	0.637 4(8)	0.122 82(20)
C(24)	0.105 7(8)	0.766 1(10)	0.133 47(24)
C(25)	0.093 6(8)	0.786 6(9)	0.163 76(24)
C(26)	0.096 2(9)	0.679 9(11)	0.184 20(20)
C(27)	0.111 9(8)	0.549 8(9)	0.173 68(18)
C(29)	0.765 7(6)	0.100 3(7)	0.205 40(16)
C(30)	0.742 3(7)	0.005 7(8)	0.226 84(16)
C(31)	0.838 9(9)	−0.069 9(9)	0.245 76(18)
C(32)	0.958 9(9)	−0.047 4(10)	0.243 58(20)
C(33)	0.980 8(8)	0.047 2(11)	0.222 22(22)
C(34)	0.886 6(7)	0.121 2(9)	0.203 32(18)
C(36)	0.607 6(6)	0.322 2(8)	0.210 35(15)
C(37)	0.688 5(7)	0.344 6(9)	0.239 92(17)
C(38)	0.663 6(8)	0.446 4(10)	0.259 77(18)
C(39)	0.562 0(7)	0.525 9(10)	0.250 01(19)
C(40)	0.478 5(8)	0.502 7(10)	0.220 81(19)
C(41)	0.501 8(7)	0.400 4(9)	0.201 22(18)
N(1)	0.686 6(5)	−0.280 8(6)	0.136 18(14)
C(43)	0.747 2(8)	−0.244 4(8)	0.170 80(18)
C(44)	0.769 0(9)	−0.363 5(10)	0.193 28(19)
C(45)	0.564 7(7)	−0.352 2(9)	0.132 86(20)
C(46)	0.469 9(8)	−0.278 6(9)	0.146 01(24)
C(47)	0.661 2(8)	−0.150 3(8)	0.116 95(21)
C(48)	0.775 5(9)	−0.072 5(10)	0.114 79(25)
C(48)	0.775 1(7)	−0.370 8(8)	0.124 27(18)
C(50)	0.733 0(10)	−0.406 1(11)	0.088 78(21)

Atoms N(1), C(43)—C(50) comprise the tetraethylammonium cation.

(0.24 g) in propan-2-ol (20 cm^3) was added $HS_2P(OPr^i)_2$ (1.3 g). The mixture was then stirred and refluxed for 15 min, during which time the ZnO slowly dissolved. The solution was then filtered and cooled, affording colourless crystals of $[Zn\{S_2P(OPr^i)_2\}_2]$ (yield 1.30 g, 90%) which were collected by filtration and washed with propan-2-ol.

Reaction of ZnO *with* $[NH_4][S_2P(OPr^i)_2]$. A mixture of ZnO (0.24 g) and $[NH_4][S_2P(OPr^i)_2]$ (1.4 g) was stirred and refluxed in propan-2-ol for 17 h. The clear solution was then filtered and cooled, the colourless crystals of $[Zn\{S_2P(OPr^i)_2\}_2]$ (yield 1.30 g, 90%) being collected by filtration and washed with propan-2-ol.

$[Zn(S_2PPh_2)_2]$. A methanolic solution of HS_2PPh_2 (1.25 g) was added slowly to a gently heated, concentrated aqueous solution of $Zn(O_2CMe)_2{\cdot}4H_2O$ (0.64 g). The precipitate of the complex which formed was collected by filtration and washed with methanol.

$[Zn(S_2PEt_2)_2]$. To an aqueous solution of $ZnSO_4{\cdot}7H_2O$ (0.4 g) was added an aqueous solution of $Na[S_2PEt_2]{\cdot}2H_2O$ (1.0 g) slowly, with stirring and heating. The precipitate of the complex which formed was filtered off and washed with propan-2-ol.

$[Zn(NC_5H_5)(S_2PPh_2)_2]$. A methanolic solution of $[C_5H_5NH][S_2PPh_2]$ (1.1 g) was added slowly, with stirring, to a concentrated aqueous solution of $Zn(O_2CMe)_2{\cdot}4H_2O$ (0.65 g). The solution which formed was concentrated *in vacuo* and crystals of the complex precipitated slowly. The complex was filtered off and washed with methanol (quantitative yield).

$[NBu^n_4][ZnI_2\{S_2P(OPr^i)_2\}]$. To a solution of $[NBu^n_4][S_2P(OPr^i)_2]$ (2.3 g) in propan-2-ol was added a solution of ZnI_2 (1.6 g) in the same solvent. The reaction mixture was stirred briefly and then allowed to stand for 30 min. The complex formed slowly as white needle-shaped crystals which were collected by filtration and washed with propan-2-ol (yield 3.0 g, 80%).

$[NEt_4][ZnI_2(S_2PPh_2)]$. To a solution of ZnI_2 (1.6 g) in acetone was added a hot solution of $[NEt_4][S_2PPh_2]$ (1.9 g) in acetone. The mixture was stirred and heated for 15 min, the solvent was then evaporated *in vacuo* and the remaining oil dissolved in a mixture of acetone and propan-2-ol (1 : 1 v/v). The complex formed slowly as white crystals and was filtered off and washed with acetone (yield 2.8 g, 80%).

$[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$. The complex $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ (3.4 g) was dissolved in propan-2-ol and and added, slowly with stirring and gentle heating (steam-bath), to a suspension of $[NMe_4][S_2P(OC_6H_4Me\text{-}p)_2]$ (1.9 g) in propan-2-ol. On cooling, flaky crystals of the complex formed and were filtered off. These could be recrystallised from toluene (yield 2.1 g, 40%).

$[NEt_4][Zn(S_2PPh_2)_3]$. A mixture of $[Zn(S_2PPh_2)_2]$ (2.8 g) and $[NEt_4][S_2PPh_2]$ (1.9 g) was refluxed in acetone (50 cm^3) for 4 h. The solution was then filtered and allowed to stand. The complex gradually crystallised, and was collected by filtration to give white crystals (yield 1.9 g, 40%).

$[NEt_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2(S_2CNMe_2)]{\cdot}2H_2O$. To a solution of $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ (2.3 g) in propan-2-ol was added, slowly and with stirring, a solution of $[NEt_4][S_2CNMe_2]$ (0.8 g) in the same solvent. The complex crystallised as white needles, and was collected by filtration (yield 1.3 g, 45%).

$[NMe_4][Zn(S_2PPh_2)_2(S_2CNMe_2)]$. A mixture of $[Zn(S_2PPh_2)_2]$ (2.8 g) and $[NMe_4][S_2CNMe_2]$ (1.1 g) was refluxed in acetone (50 cm^3) for 2 h. The solution was filtered while hot and evaporated to low bulk *in vacuo*. White needle-shaped crystals of the complex slowly formed and were collected by filtration and washed with acetone (yield 1.6 g, 40%).

Reaction of $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ *with* $[NMe_4][OCOC_{17}H_{35}]$ ($OCOC_{17}H_{35}$ = *stearate*). A solution of $[NMe_4][OCOC_{17}H_{35}]$ (0.9 g) in propan-2-ol was added slowly, and with stirring, to $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_2]$ (1.7 g) in

Table 6. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for [NMe_4][Zn{$S_2P(OC_6H_4Me$-*p*$)_2$}$_3$] (1) and [NEt_4][Zn($S_2PPh_2)_3$] (2)

	(1)	(2)		(1)
Zn(1)-S(1)	2.423(4)	2.449(2)	P(1)-O(1)	1.621(9)
Zn(1)-S(2)	2.423(4)	2.453(2)	P(1)-O(2)	1.579(9)
Zn(1)-S(3)	2.308(4)	2.305(2)	P(2)-O(3)	1.578(10)
Zn(1)-S(4)	3.565(4)	3.580(3)	P(2)-O(4)	1.611(9)
Zn(1)-S(5)	2.296(4)	2.306(2)	P(3)-O(5)	1.601(9)
Zn(1)-S(6)	3.511(4)	3.393(2)	P(3)-O(6)	1.594(9)
P(1)-S(1)	1.978(5)	2.005(3)		
P(1)-S(2)	1.961(5)	2.001(3)		(2)
P(2)-S(3)	1.986(6)	2.053(3)	P(1)-C(1)	1.814(7)
P(2)-S(4)	1.921(5)	1.951(3)	P(1)-C(8)	1.800(7)
P(3)-S(5)	1.987(5)	2.030(3)	P(2)-C(15)	1.818(7)
P(3)-S(6)	1.927(5)	1.961(3)	P(2)-C(22)	1.831(7)
O(1)-C(1)	1.401(14)		P(3)-C(29)	1.814(7)
O(2)-C(8)	1.369(14)		P(3)-C(36)	1.816(7)
O(3)-C(15)	1.368(16)			
O(4)-C(22)	1.404(15)			
O(5)-C(29)	1.430(15)			
O(6)-C(36)	1.389(15)			

	(1)	(2)		(1)		(2)
S(1)-Zn(1)-S(2)	85.48(13)	84.01(7)	S(1)-P(1)-O(1)	106.1(4)	S(1)-P(1)-C(1)	110.9(3)
S(1)-Zn(1)-S(3)	118.86(15)	108.12(7)	S(1)-P(1)-O(2)	112.5(4)	S(1)-P(1)-C(8)	110.4(3)
S(1)-Zn(1)-S(5)	105.28(14)	109.86(7)	S(2)-P(1)-O(1)	113.0(4)	S(2)-P(1)-C(1)	110.2(3)
S(2)-Zn(1)-S(3)	105.01(15)	107.16(7)	S(2)-P(1)-O(2)	107.9(4)	S(2)-P(1)-C(8)	110.7(3)
S(2)-Zn(1)-S(5)	118.15(15)	117.39(7)	O(1)-P(1)-O(2)	103.7(5)	C(1)-P(1)-C(8)	104.6(3)
S(3)-Zn(1)-S(5)	119.63(16)	123.15(8)	S(3)-P(2)-O(3)	107.6(4)	S(3)-P(2)-C(15)	107.7(2)
Zn(1)-S(1)-P(1)	80.46(16)	82.85(9)	S(3)-P(2)-O(4)	100.9(4)	S(3)-P(2)-C(22)	103.1(2)
Zn(1)-S(2)-P(1)	80.76(17)	82.83(9)	S(4)-P(2)-O(3)	112.6(4)	S(4)-P(2)-C(15)	112.1(3)
Zn(1)-S(3)-P(2)	102.29(20)	100.19(10)	S(4)-P(2)-O(4)	115.2(4)	S(4)-P(2)-C(22)	112.3(3)
Zn(1)-S(5)-P(3)	100.57(20)	100.16(10)	O(3)-P(2)-O(4)	99.2(5)	C(15)-P(2)-C(22)	103.5(3)
S(1)-P(1)-S(2)	113.24(23)	109.96(12)	S(5)-P(3)-O(5)	106.7(4)	S(5)-P(3)-C(29)	106.5(3)
S(3)-P(2)-S(4)	119.09(25)	116.99(13)	S(5)-P(3)-O(6)	100.1(4)	S(5)-P(3)-C(36)	108.1(2)
S(5)-P(3)-S(6)	119.15(25)	114.32(12)	S(6)-P(3)-O(5)	113.1(4)	S(6)-P(3)-C(29)	111.7(3)
P(1)-O(1)-C(1)	126.7(7)		S(6)-P(3)-O(6)	115.0(4)	S(6)-P(3)-C(36)	111.1(3)
P(1)-O(2)-C(8)	129.2(8)		O(5)-P(3)-O(6)	100.4(5)	C(29)-P(3)-C(36)	104.5(3)
P(2)-O(3)-C(15)	126.5(8)					
P(2)-O(4)-C(22)	122.1(8)					
P(3)-O(5)-C(29)	125.4(8)					
P(3)-O(6)-C(36)	122.4(8)					

propan-2-ol. A precipitate, probably basic zinc stearate, formed and was filtered off, leaving a clear solution which was allowed to stand at room temperature for 24 h. After this time, the colourless crystals of [NMe_4][Zn{$S_2P(OC_6H_4$-Me-*p*$)_2$}$_3$] (yield 0.7 g, 25%) which had formed were filtered off and washed in the propan-2-ol. The mother-liquor was then evaporated *in vacuo* to low bulk, and crystals of [NMe_4]-[$S_2P(OC_6H_4Me$-*p*$)_2$] (yield 0.3 g, 30%) were obtained.

Reaction of [Zn($S_2PPh_2)_2$] *with* [NEt_4][$OCOC_{17}H_{35}$]. A mixture of [Zn($S_2PPh_2)_2$] (2.8 g) and [NEt_4][$OCOC_{17}H_{35}$] (2.1 g) in acetone (50 cm^3) was refluxed for 24 h. The procedure described above was followed, and [NEt_4][Zn($S_2PPh_2)_3$] (yield 0.9 g, 20%) and [NEt_4][S_2PPh_2] (yield 0.3 g, 15%) were isolated.

Crystallographic Studies.—Crystal data. [NMe_4][Zn{S_2P-$(OC_6H_4Me$-*p*$)_2$}$_3$], $C_{46}H_{54}NO_6P_3S_6Zn$, M = 1 067.6, crystallises from toluene as irregular colourless plates, crystal dimensions 0.23 × 0.44 × 0.09 mm, monoclinic, a = 29.311(9), b = 11.032(3), c = 17.515(5) Å, β = 106.83(2)°, U = 5 421(3) Å^3, D_m = 1.32, Z = 4, D_c = 1.308 g cm^{-3}, space group $P2_1/a$ (non-standard setting of $P2_1/c$, no. 14, C_{2h}^5), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 8.11 cm^{-1}, $F(000)$ = 2 224.

Three-dimensional *X*-ray diffraction data were collected in the range 6.5 < 2θ < 50° on a Stoe Stadi-2 diffractometer by the ω-scan method. 2 490 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by Patterson image-seeking methods (using the cation ZnS_6 skeleton determined from the structure determined below) and by Fourier methods and refined by block-diagonal least-squares. Hydrogen atoms were detected and placed in calculated positions [C–H 0.95 Å, C–C–H(methyl) 110°]; their contributions were included in structure factor calculations (B = 10.0 Å^2) but no refinement of positional parameters was permitted. The cation was found to be disordered with two orientations about an approximately common centre. The disorder parameter was refined (0.679 : 0.321) and the geometries were constrained (T_d symmetry, N–C 1.48 Å); hydrogen atoms were not positioned. Refinement converted at R 0.0532 with allowance for anisotropic thermal motion of all non-hydrogen atoms with exception of those of the lower occupancy cation and for the anomalous scattering of zinc, sulphur, and phosphorus. Table 4 lists the atomic positional parameters with estimated standard deviations.

[NEt_4][Zn($S_2PPh_2)_3$], $C_{44}H_{50}NP_3S_6Zn$, M = 944.9, crystallises from acetone as colourless eight-faced columnar needles, crystal dimensions 0.14 × 0.49 × 0.17 mm, monoclinic, a = 11.160(6), b = 9.962(5), c = 43.11(3) Å, β = 104.73(5)°,

$U = 4\,635(4)$ Å^3, $D_m = 1.35$, $Z = 4$, $D_c = 1.354$ g cm^{-3}, space group $P2_1/c$ (no. 14, C^5_{2h}), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 9.33 cm^{-1}, $F(000) = 1\,968$.

The data were collected ($6.5 < 2\theta < 50°$) and processed (3 304 independent reflections) and the structure solved (Patterson and Fourier methods) and refined (R 0.0411) as for the related complex above. The cation was ordered, no geometric constraints were applied, and all hydrogen atoms were positioned ($B = 8.0$ Å^2). Table 5 lists atomic positions with estimated standard deviations.

Scattering factors were taken from ref. 11; unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

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References

1 Part 3, J. A. McCleverty, S. Gill, R. S. Z. Kowalski, N. A. Bailey, H. Adams, K. W. Lumbard, and M. A. Murphy, *J. Chem. Soc., Dalton Trans.*, 1982, 493.

2 J. A. McCleverty, N. Spencer, N. A. Bailey, and S. L. Shackleton, *J. Chem. Soc., Dalton Trans.*, 1980, 1939.

3 J. A. McCleverty, N. J. Morrison, N. Spencer, C. C. Ashworth, N. A. Bailey, M. R. Johnson, J. M. A. Smith, B. A. Tabbiner, and C. R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1980, 1945.

4 C. Glidewell, *Inorg. Chim. Acta*, 1977, **24**, 255; **25**, 159.

5 R. S. Z. Kowalski, N. A. Bailey, R. Mulvaney, H. Adams, D. A. O'Cleirigh, and J. A. McCleverty, *Transition Met. Chem.*, 1981, **6**, 64.

6 K. A. Fraser and M. M. Harding, *Acta Crystallogr.*, 1967, **22**, 75.

7 L. A. Brooks, *Rubber Chem. Technol.*, 1963, **36**, 887.

8 J. M. Hope, R. L. Martin, D. Taylor, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1977, 99.

9 T. V. Evgen'evich, *Mater. Vses. Nauchn. Konf.: Khim.*, 13th, 1975, 12; *Chem. Abstr.*, 1977, **86**, 64832.

10 A. Nieuwpoort, A. H. Dix, P. A. T. Porskamp, and J. G. M. Vander Linden, *Inorg. Chim. Acta*, 1979, **35**, 221.

11 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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