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 $[NMe_4][Zn\{S_2P(OC_6H_4Me-p)_2\}_3]$ and $[NEt_4][Zn(S_2PPh_2)_3]$ [†]

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The complexes $[NMe_4][Zn{S_2P(OC_6H_4Me-p)_2}_3]$ and $[NEt_4][Zn(S_2PPh_2)_3]$ have been prepared by treatment of $[Zn(S_2PR_2)_2]$ with $[NR'_4][S_2PR_2]$ ($R = OC_6H_4Me-p$ or Ph, R' = Me or Et). Preparation of $[Znl_2{S_2P(OPr')_2}]^-$ and $[Zn(S_2PR_2)_2(S_2CNMe_2)]^-$ ($R = OC_6H_4Me-p$ or Ph) is also described. From reactions of $[Zn{S_2P(OR)_2}_2]$ (R = Pr' or C_6H_4Me-p) with H_2O_2 or Bu'O(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') in solution to give amongst other products $[Zn{S_2P(OPh)_2}_2]$ and $[S_2P(OR)_2]^-$ with loss of phenol. The ³¹P 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: $[NMe_4][Zn{S_2P(OC_6H_4Me-p)_2}_3]$ is monoclinic with a = 29.311(9), b = 11.032(3), c = 17.515(5) Å, $\beta = 106.83(2)^\circ$, 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, $\beta = 104.73(5)^\circ$, 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 Cd¹¹ 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 dialkyland diaryl-dithiophosphate [S₂P(OR)₂] and -phosphinate [S₂PR₂] 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 ³¹P 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 dithiocarbamato- and benzothiazole-2-thiolatorelated

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 [S₂P(OR)₂]⁻, and whether anionic complexes of the type [Zn{S₂P(OR)₂}]⁻ or [Zn(S₂PR₂)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 ³¹P 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 (\neg S₂CNR₂)₂ and benzothiazole-2-sulphenamides C₇H₄NS₂–NR₂ (R = alkyl), S₈, and stearic acid are allowed to react at *ca.* 140 °C to form the ' sulphurating agent.' This is, in effect, activation of S₈ prior to attack on the rubber hydrocarbon. We have shown ^{2,3} that ZnO reacts with (\neg S₂CNR₂)₂ or C₇H₄NS₂–NR₂ (R = alkyl) to give [Zn(S₂CNR₂)₂] or [{Zn(C₇H₄NS₂)₂]_n], and that these complexes react further with stearate anion (as a quaternary ammonium salt) to give [Zn(S₂CNR₂)₃]⁻ and [Zn(C₇H₄NS₂)₃(H₂O)]⁻.

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)(OPr¹)₂ in refluxing propan-2-ol, $[Zn{S_2P(OPr^1)_2}_2]$ was obtained in good

[†] 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 (%)

		Calc.			Found			
Compound	Ċ	Н	N	S	С	н	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	а	37.0	8.5	5.4	а
$[NMe_4][S_2P(OPr^1)_2]$	41.8	9.1	4.9	а	41.2	9.1	4.9	а
$[NBu^{n}][S_{2}P(OPr^{i})_{2}]$	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
$[NMe_4][S_2P(OC_4H_4Me_p)_2]$	56.4	6.8	3.7	16.7	56.3	6.7	3.7	16.7
[NMe_][S,PPh_]	59.4	6.9	4.3	19.8	60.7	6.6	4.5	21.4
[C.H.NH][S,PPh,]	62.0	4.9	4.3	19.5	62.2	4.9	4.2	19.6
$[Zn{S_{2}P(OPr^{1})_{2}}]^{b}$	29.3	5.7	а	26.1	28.9	5.5	а	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
$[Zn{S_{2}P(OC_{c}H_{A}Me-p)_{2}}]$	48.9	4.1	a	18.7	48.7	3.8	a	18.9
$[NBu^n][ZnI_{2}{S_{2}P(OPr^{1})_{2}}]^{c}$	34.1	6.5	1.8	8.3	34.5	6.7	1.7	8.1
[NEt_][ZnL ₂ (S ₂ PPh ₂)] ⁴	34.4	4.3	2.0	9.2	35.0	4.6	2.0	9.0
$[NMe_1][Zn{S_2P(OC_1H_1Me_p)_2}_1]$	51.8	5.1	1.3	18.0	51.2	5.3	1.3	18.3
[NEt ₄][Zn(S ₂ PPh ₂) ₃]	56.0	5.3	1.5	20.4	56.2	5.6	1.6	20.4
$[NEt_1][Zn{S_P(OC_{e}H_{e}Me-p)_{2}}(S_{e}CNMe_{2})] \cdot 2H_{e}O$	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 $[NH_4][S_2P(OPr^1)_2]$. In this last reaction, ammonia must be evolved, but we found no evidence for $[Zn(NH_3)_2\{S_2P(OPr^1)_2\}_2]$. This is not surprising since the bis(ammoniate), synthesised independently by addition of ammonia to $[Zn\{S_2P(OPr^1)_2\}_2]$, is thermally labile, readily losing NH₃ to regenerate the bis(dithiophosphate) complex. Pyridine also forms a bis adduct, but dicyclohexylamine afforded only $[NH_2(C_6H_{11})_2][S_2P(OPr^1)_2]$ when it reacted with $[Zn\{S_2P(OPr^1)_2\}_2]$. The diphenyldithiophosphinato-complex $[Zn(NC_5H_5)(S_2PPh_2)_2]$, which is analogous to $[Zn(NC_5H_5)NH]-(S_2CNMe_2)_2]$, which is not surprise 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 dithiophosphinatoanions 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 Pr¹) 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 Buⁿ) or $[Zn(S_2-PEt_2)_2]$ with $[NEt_4][S_2PEt_2]$ afforded only colourless oils. However, we were able to synthesise crystalline $[NMe_4]-[Zn{S_2P(OC_6H_4Me-p)_2}_3]$ 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 $[Zn\{S_2P(OC_6H_4Me-p)_2\}_2]$ with 2 mol of $[NMe_4][OCOC_{17}H_{35}]$ caused an immediate precipitation of zinc stearate, and $[NMe_4][S_2P(OC_6H_4Me-p)_2]_2]$ 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 $[NMe_4][Zn\{S_2P(OC_6H_4Me-p)_2\}_3]$ began to form. From this reaction mixture $[NMe_4][S_2P(OC_6H_4-Me-p)_2]_2]$ was also obtained. In our previous study of the reactions of $[Zn(S_2CNR_2)_2]$ with $[NR'_4][OCOR'']$ (R'' = Me, Et, Prⁿ, Buⁿ, C₅H₁₁, C₉H₁₉, or C₁₇H₃₅) we had observed ² that 1:1 carboxylate adducts were formed with R'' = Me, Et, Prⁿ, and Buⁿ, but with R'' = Buⁿ and higher fatty acid salts, $[Zn(S_2CNR_2)_3]^-$ was formed. A comparable investigation of the behaviour of $[Zn\{S_2P(OC_6H_4Me-p)_2\}_2]$ 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 $[Zn\{S_2P(OC_6H_4Me-p)_2\}_2]$ and $[Zn-(S_2PPh_2)_2]$ with the appropriate salts of $[S_2CNMe_2]^-$ did indeed afford $[NMe_4][Zn\{S_2P(OC_6H_4Me-p)_2\}_2(S_2CNMe_2)]$ (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 $[NMe_4][S_2P(OC_6H_4Me-p)_2]$. 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)NR₂₂] or [Zn{SO₂C(S)NR₂₂].⁷ Accordingly, we investigated the behaviour of dithiophosphato-species with H₂O₂ or Bu^tO(OH) in water giving, not surprisingly, $[-S_2P(OR)_2]_2$. Treatment of $[Zn{S_2P(OR)_2}]$ (R = Pr⁴ or C₆H₄Me-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 $[Zn{S_2P(OC_6H_4Me-p)_2}_2]$ was treated with two mol of Bu'O(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 $[Zn_2\{S_2P(OC_6H_4Me-p)_2\}_3(OH)]$. The i.r. spectrum of this compound is very similar to that of [Zn- $\{S_2P(OC_6H_4Me-p)_2\}_2$ but has additional strong bands at 1 200 and 675 cm⁻¹. We have discounted the possibility that the compound is $[Zn{SOP(=S)(OC_6H_4Me-p)_2}_2]$ (having an S=O group) or $[Zn{OSP(=S)(OC_6H_4Me-p)_2}_2]$ 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 Me₂SO 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 $[Zn{S_2P(OC_6H_4Me-p)_2}_2]$ was treated with four mol equivalents of Bu'O(OH) in the absence of water, $[-S_2P(OC_6H_4-Me-p)_2]_2$ and ZnSO₄ 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 [NMe4][OH] [NMe₄][S₂P(OEt)₂] and not [NMe₄][S₂P(OPh)₂] was isolated in good yield. Similarly, when $[Zn{S_2P(OPh)_2}_2]$ was treated with [NMe₄][S₂P(OPh)₂] in propan-2-ol, needle-shaped crystals, presumably of [NMe4][Zn{S2P(OPh)2}3] formed initially, but redissolved. After 4 weeks, rhombic crystals of [Zn- $\{S_2P(OPr^1)_2\}_2$] 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 Prⁱ), and the smell of phenol could be detected in the reaction mixture. However, [NR'4][S2P(OPh)2] was quite stable under these conditions. Furthermore, we observed that [NMe4]- $[Zn{S_2P(OC_6H_4Me-p)_2}_3]$ could be recrystallised from propan-2-ol, and $[Zn{S_2P(OC_6H_4Me-p)_2}_2]$ 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 substitution⁹ 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



Scheme. R = alkyl, R' = aryl.

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 S₂P(OC₆-H₄Me-*p*)₂ relative to H in S₂P(OPh)₂, or the negative charge on the anion. In each case, the P atom will carry more charge

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

Compound	δ(³¹ P) "	Solvent
[NMe_][S_P(OMe)_]	118.9	$(CD_{1})_{1}CO_{1}$
[NMe ₄][S ₂ P(OEt) ₂]	114.1	$(CD_{1})_{CO}$
$[NMe_{1}][S_{2}P(OPr^{i})_{2}]$	113.2	$(CD_{1})_{CO}$
$[NH_3(C_6H_{11})][S_2P(OPr^1)_3]$	107.0	CD ₂ Cl ₂
$[NH_2(C_4H_{11})_2][S_2P(OPr^4)_2]$	108.4	CD ₂ Cl ₂
$[NMe_{4}][S_{2}P(OC_{6}H_{4}Me_{7})_{2}]$	108.8	(CD ₄) ₂ CO
$[Zn{S_2P(OMe)_2}]$	104.1	CDCl ₃
$[Zn{S_2P(OEt)_2}]$	98.6	CDCl ₁
$[Zn{S_2P(OPr^i)_2}_2]$	94.5	CDCl ₃
	94.2	CD ₂ Cl ₂
$[Zn{S_2P(OC_6H_4Me-p)_2}_2]$	96.5	CDCl ₁
$[Zn{S_2P(OMe)_2}_2] +$	108.2	CDCl ₃
$[NMe_4][S_2P(OMe)_2](1:1)$		
$[Zn{S_2P(OEt)_2}] +$	104.5	CDCl ₃
$[NMe_4][S_2P(OEt)_2](1:1)$		-
$[Zn{S_2P(OPr^i)_2}_2] +$	100.3	CDCl ₃
$[NMe_4][S_2P(OPr^i)_2](1:1)$		
$[Zn{S_2P(OPr^i)_2}_2] +$	98.1	CD_2Cl_2
$[NH_3(C_6H_{11})][S_2P(OPr^i)_2](1:1)$		
$[Zn{S_2P(OPr^i)_2}_2] +$	97.8	CD_2Cl_2
$[NH_2(C_6H_{11})_2][S_2P(OPr^i)_2](1:1)$		
$[Zn{S_2P(OC_6H_4Me-p)_2]_2] +$	100.6	CD_2Cl_2
$[NMe_4][S_2P(OC_6H_4Me_p)_2](1:1)$		
	101.8 °	CD_2Cl_2
$[NMe_4][Zn\{S_2P(OC_6H_4Me_p)_2\}_3]^{c}$	100.3	CD_2Cl_2
$[NBu^{n}_{4}][ZnI_{2}\{S_{2}P(OPr^{i})_{2}\}]$	94.7	(CD ₃) ₂ CO
$[NEt_4][Zn{S_2P(OC_6H_4Me-p)_2}_2-$	101.4	(CD ₃) ₂ CO
$(S_2CNMe_2)]$		
$[NMe_4][S_2PEt_2]$	73.3	CDCl ₃
$[Zn(S_2PEt_2)_2]$	80.7	CDCl ₃
[C ₅ H ₅ NH][S ₂ PPh ₂]	61.3	CDCl ₃
$[Zn(S_2PPh_2)_2]$	62.8	CDCl ₃
[NEt_][Zn(S,PPh_)]	61.6	CDCh

^a In p.p.m., relative to 85% H₃PO₄, 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.

relative to that in $S_2P(OPh)_2$, thus inhibiting nucleophilic attack by ROH.

We also noted that $HSP(S)(OPh)_2$, $[-S_2P(OPh)_2]_2$, and mixtures of $[Zn{S_2P(OPr^1)_2}_2]$ and $[NMe_4][S_2P(OR)_2]$ (R = Ph or C₆H₄Me-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.—Glidewell⁴ has shown that the chemical shift of the P atom in S₂P(OR)₂ is sensitive to the nature of, and to the group attached to, the S atoms of the dithiophosphato-group. Thus $\delta^{(31P)}$ for ionic species, [S₂P(OR)₂]⁻, is significantly different, and generally to lower field, of that found for neutral covalent metal-containing species, [M{S₂P(OR)₂}_n].

In Table 2 are given the ³¹P 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 $\delta^{(31P)}$ 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 H₃PO₄), the actual position of the signal being in-

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

Ratio	δ(³¹ P) ^a /p.p.m.
1:10	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 CD₂Cl₂, relative to 85% H₃PO₄, ± 1 p.p.m. ^b Solution made up from isolated [NMe₄][Zn{S₂P(OC₆H₄Me-*p*)₂}]. ^c In (CD₃)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 $[NMe_4][Zn\{S_2P(OC_6H_4Me_{-p})_2\}_3]$ and the 1 : 1 mixture of $[NMe_4][S_2P(OC_6H_4Me_{-p})_2]$ are identical (within the experimental error).

These data strongly suggest that $[NMe_4][Zn{S_2P(OC_6H_4-Me-p)_2}_3]$ dissociates rapidly in solution, and it seems probable that the equilibrium shown below is established in which

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

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 ³¹P resonances, but the observed single ³¹P 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 $[NMe_4][S_2P(OC_6H_4Me-p)_2]$ and $[Zn\{S_2P(OC_6H_4Me-p)_2\}_2]$ 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 $[NMe_4][S_2P(OC_6H_4Me-p)_2]$ 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 ³¹P resonances were also detected in solutions of $[NMe_4][Zn{S_2P(OC_6H_4Me-p)_2}_3]$ in chloroform and acetone.

Molecular Structures of $[NMe_4][Zn{S_2P(OC_6H_4Me-p)_2}_3]$ 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 dis-



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



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

tance 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.

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 $[Zn{S_2P(OC_6H_4Me-p)_2}_3]^-$ anion, the bond angles at the oxygen atoms are large at $125.7 \pm 3.5^\circ$ 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 $[Zn{S_2P(OC_6H_4Me-p)_2}_3]^-$ the Zn-S and S-P bond lengths are greater by approximately $0.04 \text{ Å} (\sim 8\sigma)$. 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-thiolatoanalogues. There are certain small differences in detail, the most significant being structural. However, the variations in geometries between $[Zn(S_2CNMe_2)_3]^-$, $[Zn(C_7H_4NS_2)_3^ (H_2O)]^-$, $[Zn\{S_2P(OC_6H_4Me-p)_2\}_3]^-$, and $[Zn(S_2PPh_2)_3]^-$ can **Table 4.** Atomic positional parameters with estimated standard deviations in parentheses for $[NMe_4][Zn{S_2P(OC_6H_4Me-p)_2}_3]$

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)	-0.3334(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)	-0.2772(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)	-0.2014(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)	0.1810(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)	-0.0681(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)	-0.1619(7)	N(1)	-0.3118(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)	-0.2933(9)	0.384 2(16)	-0.0113(13)
C(12)	0.543 8(4)	0.422 2(12)	-0.162 1(7)	C(45)	-0.2963(9)	0.168 0(18)	-0.0344(12)
C(13)	0.523 6(4)	0.375 4(12)	-0.106 4(8)	C(46)	-0.3645(3)	0.271 5(26)	-0.0141(13)
C(14)	0.578 1(6)	0.408 8(15)	-0.2750(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)	-0.2437(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)	-0.3220(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 Buⁿ; R = Me, Et, Pr¹, Ph, or C₆H₄Me-p). To a solution of HS₂P(OR)₂ (0.1 mol) in toluene (50 cm³) 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 cm³), 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%).

 $[C_{5}H_{5}NH][S_{2}PPh_{2}]$. To a solution of $HS_{2}PPh_{2}$ (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%).

 $[Zn{S_2P(OC_6H_4Me-p)_2}_2]$. To a suspension of P_4S_{10} (11.1 g) in toluene (60 cm³) was added a solution of *p*-MeC₆H₄OH (22 g) in toluene (10 cm³). The mixture was then refluxed until a clear solution had formed, when the solvent was evaporated *in vacuo* affording HS_2P(OC₆H₄Me-p)₂ (yields 80–90%).

To a solution of $HS_2P(OC_6H_4Me-p)_2$ (31.0 g) in toluene (60 cm³) at room temperature was added an aqueous solution of ZnSO₄·7H₂O (14.4 g). The mixture was stirred vigorously overnight, the organic layer was then separated, washed with water (2 × 30 cm³), 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 HS₂P(OPr¹)₂. To a suspension of ZnO

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z c
Zn(1)	0.393 35(8)	0.174 35(9)	0.119 68(2)	C(22)	0.125 9(6)	0 530 6(7)	0 143 19(16)
S(1)	0.229 95(17)	0.02492(21)	0.089 90(4)	C(23)	0.1215(7)	0.637.4(8)	0.122.82(20)
S(2)	0.485 03(17)	0.136 72(21)	0.074 38(4)	C(24)	0.105 7(8)	0.7661(10)	0.133 47(24)
S(3)	0.316 58(17)	0.390 24(20)	0.115 06(4)	C(25)	0.093 6(8)	0.786 6(9)	0.163 76(24)
S(4)	0.164 90(21)	0.227 76(24)	0.163 57(5)	C(26)	0.096 2(9)	0.679 9(11)	0.184 20(20)
S(5)	0.491 21(17)	0.077 97(20)	0.168 14(4)	C(27)	0.111 9(8)	0.549 8(9)	0.173 68(18)
S(6)	0.686 70(19)	0.292 58(20)	0.146 43(4)	C(29)	0.765 7(6)	0.100 3(7)	0.205 40(16)
P(1)	0.328 62(17)	0.033 31(20)	0.057 04(4)	C(30)	0.742 3(7)	0.005 7(8)	0.226 84(16)
P(2)	0.158 36(17)	0.362 32(21)	0.130 28(4)	C(31)	0.838 9(9)	-0.069 9(9)	0.245 76(18)
P(3)	0.639 88(17)	0.201 61(20)	0.181 94(4)	C(32)	0.958 9(9)	-0.047 4(10)	0.243 58(20)
C (1)	0.364 1(7)	-0.133 9(7)	0.045 29(15)	C(33)	0.980 8(8)	0.047 2(11)	0.222 22(22)
C(2)	0.308 6(8)	-0.2452(8)	0.054 38(18)	C(34)	0.886 6(7)	0.121 2(9)	0.203 32(18)
C(3)	0.338 1(9)	-0.372 1(9)	0.046 06(20)	C(36)	0.607 6(6)	0.322 2(8)	0.210 35(15)
C(4)	0.425 5(8)	-0.389 5(9)	0.028 76(20)	C(37)	0.688 5(7)	0.344 6(9)	0.239 92(17)
C(5)	0.480 3(8)	-0.279 4(9)	0.019 46(21)	C(38)	0.663 6(8)	0.446 4(10)	0.259 77(18)
C(6)	0.451 0(7)	-0.153 4(9)	0.028 02(18)	C(39)	0.562 0(7)	0.525 9(10)	0.250 01(19)
C(8)	0.238 3(6)	0.108 5(7)	0.020 59(16)	C(40)	0.478 5(8)	0.502 7(10)	0.220 81(19)
C(9)	0.243 1(7)	0.244 9(9)	0.016 09(17)	C(41)	0.501 8(7)	0.400 4(9)	0.201 22(18)
C(10)	0.173 4(8)	0.305 1(10)	$-0.011\ 13(20)$	N(1)	0.686 6(5)	-0.2808(6)	0.136 18(14)
C(11)	0.094 2(8)	0.229 5(11)	-0.034 46(20)	C(43)	0.747 2(8)	-0.2444(8)	0.170 80(18)
C(12)	0.088 1(9)	0.094 8(11)	-0.030 16(19)	C(44)	0.769 0(9)	-0.363 5(10)	0.193 28(19)
C(13)	0.160 6(8)	0.031 2(9)	-0.002 97(18)	C(45)	0.564 7(7)	-0.3522(9)	0.132 86(20)
C(15)	0.031 8(6)	0.332 1(7)	0.095 02(16)	C(46)	0.469 9(8)	-0.278 6(9)	0.146 01(24)
C(16)	0.038 8(7)	0.361 6(9)	0.064 32(17)	C(47)	0.661 2(8)	-0.150 3(8)	0.116 95(21)
C(17)	-0.0620(7)	0.337 2(10)	0.038 62(18)	C(48)	0.775 5(9)	-0.072 5(10)	0.114 79(25)
C(18)	-0.169 9(7)	0.287 5(9)	0.043 15(20)	C(48)	0.775 1(7)	-0.370 8(8)	0.124 27(18)
C(19)	-0.177 5(7)	0.258 2(9)	0.073 82(20)	C(50)	0.733 0(10)	-0.406 1(11)	0.088 78(21)
C(20)	-0.077 9(7)	0.279 4(9)	0.100 3(18)				

Table 5. Atomic positional parameters with estimated standard deviations in parentheses for [NEt₄][Zn(S₂PPh₂)₃]

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

(0.24 g) in propan-2-ol (20 cm³) was added HS₂P(OPrⁱ)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 $Zn(O_2CMe)_2$ ·4H₂O (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 $ZnSO_4$ ·7H₂O (0.4 g) was added an aqueous solution of Na[S₂PEt₂]·2H₂O (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 $[C_5H_5NH]$ -[S₂PPh₂] (1.1 g) was added slowly, with stirring, to a concentrated aqueous solution of $Zn(O_2CMe)_2$ ·4H₂O (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).

 $[NBu^{n}_{4}][ZnI_{2}{S_{2}P(OPr^{i})_{2}}]$. To a solution of $[NBu^{n}_{4}]-[S_{2}P(OPr^{i})_{2}]$ (2.3 g) in propan-2-ol was added a solution of ZnI₂ (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%).

[NEt₄][ZnI₂(S₂PPh₂)]. To a solution of ZnI₂ (1.6 g) in acetone was added a hot solution of [NEt₄][S₂PPh₂] (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%).

 $[NMe_4][Zn{S_2P(OC_6H_4Me-p)_2}_3]$. The complex $[Zn{S_2P(OC_6H_4Me-p)_2}_3]$ (3.4 g) was dissolved in propan-2-ol and and added, slowly with stirring and gentle heating (steambath), to a suspension of $[NMe_4][S_2P(OC_6H_4Me-p)_2]$ (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%).

[NEt₄][Zn(S₂PPh₂)₃]. A mixture of $[Zn(S_2PPh_2)_2]$ (2.8 g) and [NEt₄][S₂PPh₂] (1.9 g) was refluxed in acetone (50 cm³) 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%).

 $[NEt_4][Zn{S_2P(OC_6H_4Me-p)_2}_2(S_2CNMe_2)]^2H_2O.$ To a solution of $[Zn{S_2P(OC_6H_4Me-p)_2}_2]$ (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 $[Zn(S_2-PPh_2)_2]$ (2.8 g) and $[NMe_4][S_2CNMe_2]$ (1.1 g) was refluxed in acetone (50 cm³) 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 $[Zn{S_2P(OC_6H_4Me-p)_2}]$ with $[NMe_4]$ -[OCOC₁₇H₃₅] (OCOC₁₇H₃₅ = stearate). A solution of [NMe₄][OCOC₁₇H₃₅] (0.9 g) in propan-2-ol was added slowly, and with stirring, to $[Zn{S_2P(OC_6H_4Me-p)_2}]$ (1.7 g) in

		(1)	(2)		(1)	
Zn(1)	-S(1)	2.423(4)	2.449(2)	P(1)-O(1)	1.621(9)	
$Z_n(1)$	-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)-9	S(1)	1.978(5)	2.005(3)	., .,		
P(1)-	5(2)	1.961(5)	2.001(3)		(2)	
P(2)-5	S(3)	1.986(6)	2.053(3)	P(1)-C(1)	1.814(7)	
P(2)-9	5(4)	1.921(5)	1.951(3)	P(1)-C(8)	1.800(7)	
P(3)-9	S(5)	1.987(5)	2.030(3)	P(2)-C(15)	1.818(7)	
P(3)-9	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)					

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)

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 [NMe4][Zn{S2P(OC6H4- $Me-p_{2}_{3}$ (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 [NMe4]- $[S_2P(OC_6H_4Me-p)_2]$ (yield 0.3 g, 30%) were obtained.

Reaction of [Zn(S₂PPh₂)₂] with [NEt₄][OCOC₁₇H₃₅]. A mixture of [Zn(S₂PPh₂)₂] (2.8 g) and [NEt₄][OCOC₁₇H₃₅] (2.1 g) in acetone (50 cm³) was refluxed for 24 h. The procedure described above was followed, and [NEt₄][Zn(S₂PPh₂)₃] (yield 0.9 g, 20%) and [NEt₄][S₂PPh₂] (yield 0.3 g, 15%) were isolated.

Crystallographic Studies.—Crystal data. [NMe4][Zn{S2P- $(OC_6H_4Me-p)_2$], $C_{46}H_{54}NO_6P_3S_6Zn$, M = 1.067.6, crystallises from toluene as irregular colourless plates, crystal dimensions $0.23 \times 0.44 \times 0.09$ mm, monoclinic, a =29.311(9), b = 11.032(3), c = 17.515(5) Å, $\beta = 106.83(2)^{\circ}$, U = 5 421(3) Å³, $D_m = 1.32$, 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 ($\lambda = 0.71069$ Å), $\mu(Mo-K_{\alpha}) = 8.11$ cm^{-1} , F(000) = 2224.

Three-dimensional X-ray diffraction data were collected in

the range $6.5 < 2\theta < 50^\circ$ 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 leastsquares. 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 $(B = 10.0 \text{ Å}^2)$ 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.

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

U = 4.635(4) Å³, $D_m = 1.35$, Z = 4, $D_c = 1.354$ g cm⁻³, space group $P2_1/c$ (no. 14, C_{2h}^5), 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 $(6.5 \le 20 \le 50^\circ)$ 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 ($B = 8.0 \text{ Å}^2$). 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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