Reactions of $[Zn\{S_2P(OR)_2\}_2]$ with Nitrogen Bases and the Single-crystal *X*-Ray Structures of $[Zn\{S_2P(OPr^i)_2\}_2]\cdot H_2NCH_2CH_2NH_2$ and $[Zn\{S_2P(OPr^i)_2\}_2]\cdot NC_5H_5$*

Michael G. B. Drew, Masihul Hasan, Richard J. Hobson, and David A. Rice
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

The adducts $[Zn\{S_2P(OR)_2\}_2]\cdot L$ [L = $H_2NCH_2CH_2NH_2$ (en), $MeHNCH_2CH_2NHMe$ (dmen), $Me_2NCH_2CH_2NMe_2$ (tmen), 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, or pyridine; R = Et or Pr^i] and the ionic compounds $[Zn(en)_3][S_2P(OR)_2]_2$ and $[Zn(dmen)][S_2P(OR)_2]_2$ have been isolated by treating $[Zn\{S_2P(OR)_2\}_2]$ with L in the appropriate stoicheiometry. The crystal structures of $[Zn\{S_2P(OPr^i)_2\}_2]\cdot en$ (**1**) and $[Zn\{S_2P(OPr^i)_2\}_2]\cdot py$ (**2**) have been determined: (**1**), monoclinic, space group $P2_1/c$, with a = 13.402(8), b = 16.470(9), c = 12.294(7) Å, β = 99.0(1)°, and Z = 4; (**2**), monoclinic, space group $P2_1/n$ with a = 21.28(1), b = 8.35(1), c = 16.27(1) Å, β = 99.5(1)°, and Z = 4. Diffractometer data were collected for both crystals [of which 1 340 (**1**) and 1 940 (**2**) were above background] and both structures were refined to R 0.073. In (**1**) the zinc atom is four-co-ordinate forming two Zn–N bonds [2.077(13) and 1.922(16) Å] to the bidentate ethylenediamine molecule and two Zn–S bonds [2.292(5) and 2.331(5) Å] to the monodentate dithiophosphate ligands. In (**2**) the zinc atom is five-co-ordinate being bonded to pyridine [Zn–N 2.015(12) Å], and to two bidentate dithiophosphate ligands. One ligand is bonded to the metal more symmetrically [Zn–S 2.502(4) and 2.358(4) Å] than the other [Zn–S 2.269(4) and 3.032(4) Å]. The ^{31}P n.m.r. spectra of a number of these compounds have been examined. A correlation between the positions of the resonances and the mode of bonding of the $[S_2P(OR)_2]^-$ groups to the metal has been established.

Zinc dialkyl dithiophosphates are added to a number of engine oils as anti-oxidants. It is believed that they act by promoting the decomposition of hydroperoxides[1] and that the first oxidation product is the 'basic' compound $[Zn_4O\{S_2P(OR)_2\}_6]$.[2,3]

Long chain polymeric amines are added to commercial oils; these can act as Lewis bases and thus may bond to the zinc(II) centres and so modify the nature of the zinc dialkyl dithiophosphate species that is available to curtial oxidation. It is commercially important to determine the nature of the compounds in solution and so a method for correlating the position of the ^{31}P n.m.r. resonances from the dialkyl dithiophosphate residues with the mode of bonding to the metal is desirable. No single-crystal studies of adducts of $[Zn\{S_2P(OR)_2\}_2]$ have been reported, so an investigation of one or two structures of adducts with nitrogen bases is required before this correlation can be established. Furthermore, there are uncertainties concerning the nature of the pyridine adducts of $[Zn\{S_2P(OR)_2\}_2]$[4,5] with both 1:1 and 1:2 adducts being reported.

We have allowed $[Zn\{S_2P(OR)_2\}_2]$ to react with a range of nitrogen donors and carried out single-crystal *X*-ray studies on two of the products, *viz.* $[Zn\{S_2P(OPr^i)_2\}_2]\cdot py$ (py = pyridine) and $[Zn\{S_2P(OPr^i)_2\}_2]\cdot en$ (en = ethylenediamine). These structures are used to interpret ^{31}P n.m.r. studies on solutions of $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i) and their adducts. Finally, we have studied the reactions of the 'basic' compound $[Zn_4O\{S_2P(OR)_2\}_6]$ with nitrogen donors to ascertain whether or not any $[Zn_4O\{S_2P(OR)_2\}_6]$ formed by oxidation in engine oil is likely to persist in the presence of such bases.

Experimental

Preparation of Materials.—Dialkyl dithiophosphoric acids were prepared by allowing P_4S_{10} to react with ROH (R = Et, Pr^i, or Ph) under nitrogen. They were converted into ammonium salts by bubbling dry ammonia through solutions of the acids.[6]

$[Zn\{S_2P(OR)_2\}_2]$. Zinc diethyl dithiophosphate was prepared by allowing zinc sulphate (0.083 mol) to react with ammonium diethyl dithiophosphate (0.177 mol) in water (500 cm^3). The desired product formed as a white precipitate and was extracted into diethyl ether. The resulting solution was dried with magnesium sulphate and on evaporation of the solvent a white crystalline material was obtained in approximately 90% yield. This was purified by recrystallisation from light petroleum (b.p. 100—120 °C). Analytical data for this and all other compounds are given in Table 1.

Zinc di-isopropyl dithiophosphate was prepared by allowing Pr^iOH (3.9 mol) to react with P_4S_{10} (0.375 mol) over 30 min. The resulting mixture was kept at 80 °C for a further 30 min. To this warm solution was added zinc acetate dihydrate (0.60 mol) dissolved in ethanol. The mixture was stirred for 15 min and allowed to cool to room temperature during which time white crystals of the product were deposited in 67% yield.

Basic complexes $[Zn_4O\{S_2P(OR)_2\}_6]$ (R = Et, Pr^i, *or* Bu). To a solution of $[Zn\{S_2P(OR)_2\}_2]$ [for R = Et the solvent was methanol, for R = Pr^i it was light petroleum (b.p. 80—100 °C)] was added a 70% solution of 1,1-dimethylethyl hydroperoxide (molar ratio of reactants 4:1). After 1 h of continuous stirring, the product was deposited as a fine white solid. The compounds were recrystallised from light petroleum (b.p. 80—100 °C). Final yields were 62% for R = Et and 90% for R = Pr^i. The other product of the reaction was shown to be $(RO)_2P(S)SS(S)P(OR)_2$. The basic complex with R = Bu was prepared by the method given in ref. 7.

$[Zn_4O\{S_2P(OPh)_2\}_6]$. To a hot (100 °C) solution of phenol (2.34 mol) in xylene (800 cm^3) was added P_4S_{10} (0.292 mol). The temperature was raised to 140 °C and a clear solution was

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* Bis(*OO*′-di-isopropyl dithiophosphato-*S*)(ethylenediamine)zinc and bis(*OO*′-di-isopropyl dithiophosphato-*SS*′)(pyridine)zinc.

Supplementary data available (No. SUP 56500, 10 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical data (%) for zinc dialkyl dithiophosphates and their nitrogen-base complexes

	Found				Requires			
Complex	Zn	C	N	H	Zn	C	N	H
$[Zn\{S_2P(OEt)_2\}_2]$		22.0		4.7		22.05		4.65
$[Zn_4O\{S_2P(OEt)_2\}_6]$		21.1		4.4		20.75		4.35
$[Zn\{S_2P(OPr^i)_2\}_2]$	13.2	29.15		5.2	13.3	29.3		5.75
$[Zn_4O\{S_2P(OPr^i)_2\}_6]$	16.9	27.7		5.3	16.8	27.75		5.45
$[Zn_4O\{S_2P(OBu)_2\}_6]$		33.9		5.95		33.4		6.3
$[Zn_4O\{S_2P(OPh)_2\}_6]$	13.3	44.5		2.9	13.3	44.0		3.1
$[Zn\{S_2P(OEt)_2\}_2]\cdot en$		23.4	5.4	5.6		24.2	5.65	5.7
$[Zn(en)_3][S_2P(OEt)_2]_2$		27.3	13.6	7.4		27.3	13.65	7.2
$[Zn\{S_2P(OEt)_2\}_2]\cdot dmen$		27.8	5.8	6.2		27.5	5.35	6.15
$[Zn\{S_2P(OEt)_2\}_2]\cdot tmen$		30.6	5.0	6.5		30.45	5.05	6.6
$[Zn\{S_2P(OEt)_2\}_2]\cdot py$		30.4	2.7	4.9		30.3	2.7	4.9
$[Zn\{S_2P(OEt)_2\}_2]\cdot bipy$		36.6	4.7	4.7		36.55	4.75	4.75
$[Zn\{S_2P(OEt)_2\}_2]\cdot phen$		40.3	4.7	4.5		39.0	4.55	4.6
$[Zn\{S_2P(OEt)_2\}_2]\cdot dmphen$		42.6	4.4	4.8		41.0	4.35	5.0
$[Zn\{S_2P(OPr^i)_2\}_2]\cdot en$	11.7	30.5	5.2	6.5	11.85	30.45	5.05	6.6
$[Zn(en)_3][S_2P(OPr^i)_2]_2$	9.6	32.1	12.5	7.7	9.75	32.15	12.5	7.8
$[Zn(dmen)_2][S_2P(OPr^i)_2]_2$		35.9	8.4	7.0		35.95	8.4	7.85
$[Zn\{S_2P(OPr^i)_2\}_2]\cdot tmen$	10.8	35.6	4.7	7.2	10.75	35.55	4.6	7.3
$[Zn\{S_2P(OPr^i)_2\}_2]\cdot py$	11.2	35.6	2.5	5.8	11.45	33.75	2.45	5.85
$[Zn\{S_2P(OPr^i)_2\}_2]\cdot bipy$	10.0	40.9	4.4	5.5	10.1	40.75	4.3	5.6
$[Zn\{S_2P(OPr^i)_2\}_2]\cdot phen$		42.9	4.1	5.2		42.85	4.15	5.4
$[Zn\{S_2P(OPr^i)_2\}_2]\cdot dmphen$		45.8	4.2	5.5		44.6	4.0	5.75
$[Zn\{S_2P(OPh)_2\}_2]\cdot 2py$		52.0	3.6	3.4		51.9	3.55	3.85

formed within 15 min. The mixture was allowed to cool to room temperature when gaseous ammonia was passed into it for 30 min. On the addition of $[Zn(O_2CMe)_2]\cdot 2H_2O$ (0.77 mol) a clear solution formed. The mixture was heated to 80 °C and quickly poured into cold water (1 dm^3) whereupon a white precipitate of $[Zn_4O\{S_2P(OPh)_2\}_6]$ was deposited. Yield based upon $[Zn(O_2CMe)_2]\cdot 2H_2O$ was 94%.

The nitrogen-base adducts of $[Zn\{S_2P(OR)_2\}_2]$. These were obtained by allowing $[Zn\{S_2P(OR)_2\}_2]$ to react with a stoicheiometric amount of nitrogen base in a non-co-ordinating solvent such as $CHCl_3$ or light petroleum.

Physical Measurements.—Infrared spectra of Nujol mulls of the compounds were obtained using a Perkin-Elmer 683 grating spectrophotometer. Proton n.m.r. spectra of solutions in $CDCl_3$ were recorded with either a Varian T-60 or HA-100 apparatus, ^{31}P n.m.r. spectra either with a JEOL FX900 FT instrument (ESSO Abingdon Laboratory) or with a Bruker WH-90 instrument at Warwick University where Dr. J. Kisenyi kindly made the measurements.

Table 2. Crystal data for $[Zn\{S_2P(OPr^i)_2\}_2]\cdot L (L = en\ or\ py)$

	$[Zn\{S_2P(OPr^i)_2\}_2]\cdot en$	$[Zn\{S_2P(OPr^i)_2\}_2]\cdot py$
M	551.84	570.82
$F(000)$	1 160	1 181
$D_m/g\ cm^{-3}$	1.34	1.31
$D_c/g\ cm^{-3}$	1.36	1.33
μ/cm^{-1}	13.78	12.97
Approx. size of crystal/mm	1.0 × 0.4 × 0.2	0.7 × 0.35 × 0.10
$a/Å$	13.402(8)	21.28(1)
$b/Å$	16.470(9)	8.35(1)
$c/Å$	12.294(7)	16.27(1)
$\beta/°$	99.0(1)	99.5(1)
$U/Å^3$	2 680.38	2 851.69
Space group	$P2_1/c$	$P2_1/n$
Rotation axis	c	b
Number of unique reflections	2 654	3 212
Criteria for inclusion	$I > 3\sigma(I)$	$I > 4.5\sigma(I)$
Reflections used in refinement	1 340	1 940

Details common to both complexes: crystal system, monoclinic; $Z = 4$.

Single-crystal X-*Ray Determinations.*—Crystal data are given in Table 2. Intensity data were collected on a Stoe STADI-2 diffractometer with zirconium-filtered Mo-K_α radiation and ω scans of width (1.5 + 0.5 sinμ/tanθ). The scan speed was 0.033° s^{-1} and the background was measured at the ends of the ω scan for 20 s. Measurement of standard reflections showed no deterioration. Both structures were determined by heavy-atom methods. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions at 0.95 Å from the nitrogen or carbon atom to which they were bonded. The hydrogen atoms of methyl groups were allowed to refine independently but with constrained C–H, H $\cdots$ H, and H $\cdots$ C distances. Their thermal parameters were refined although those of atoms bonded to the same atom were constrained to be the same. The weighting scheme used was $w = 1/[\sigma(F) + 0.003\ F^2]$, where $\sigma(F)$ was taken from counting statistics. Scattering factors and dispersion corrections were taken from ref. 8. Calculations were carried using SHELX 76 on the Amdahl V7 at this University. Final R values were 0.073 (R' 0.075) and 0.073 (R' 0.074) for $[Zn\{S_2P(OPr^i)_2\}_2]\cdot en$ and $[Zn\{S_2P(OPr^i)_2\}_2]\cdot py$ respectively. Positional parameters are given in Tables 3 and 4 and the geometries of the metal co-ordination spheres in Table 5.

Results and Discussion

Both $[Zn\{S_2P(OPr^i)_2\}_2]\cdot en$ (**1**) and $[Zn\{S_2P(OPr^i)_2\}_2]\cdot py$ (**2**) exist as discrete molecules which are shown in Figures 1 and 2 together with the respective atomic numbering schemes.

In (**1**) the zinc atom is four-co-ordinate being bonded to two nitrogen atoms of the bidentate ethylenediamine and to two

Table 3. Atomic co-ordinates (× 10^4) for complex (**1**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Zn	5 240(1)	2 416(1)	1 479(2)
P(1)	7 131(3)	1 555(3)	313(3)
S(1)	6 762(3)	2 631(2)	898(3)
P(2)	3 051(4)	3 213(3)	429(4)
S(2)	6 148(3)	1 045(3)	−768(4)
S(3)	4 323(3)	3 624(3)	1 280(4)
S(4)	3 111(4)	2 583(4)	−852(4)
O(1)	8 177(7)	1 687(6)	−82(7)
O(2)	7 443(7)	1 026(6)	1 362(8)
O(3)	2 507(8)	2 745(7)	1 310(9)
O(4)	2 308(9)	3 985(7)	256(9)
N(1)	5 337(10)	2 049(11)	3 108(10)
N(2)	4 585(10)	1 392(10)	1 109(11)
C(1)	5 156(18)	1 177(14)	3 041(19)
C(2)	4 416(18)	949(12)	2 134(20)
C(11)	8 280(15)	1 960(12)	−1 161(14)
C(12)	8 709(17)	2 796(13)	−1 124(19)
C(13)	8 908(20)	1 353(16)	−1 646(21)
C(21)	7 826(16)	210(10)	1 279(17)
C(22)	7 165(17)	−347(11)	1 786(18)
C(23)	8 875(19)	171(15)	1 802(27)
C(31)	1 508(14)	2 432(14)	972(21)
C(32)	808(16)	2 793(15)	1 692(18)
C(33)	1 548(16)	1 544(15)	1 144(18)
C(41)	2 199(15)	4 472(14)	−671(17)
C(42)	2 919(17)	5 155(13)	−624(21)
C(43)	1 124(18)	4 707(16)	−887(24)

Table 4. Atomic co-ordinates (× 10^4) for complex (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Zn	−1 455(1)	1 856(2)	586(1)
S(1)	−2 582(2)	2 227(4)	−120(2)
S(2)	−1 576(2)	−781(4)	66(3)
S(3)	−175(2)	805(4)	1 536(2)
S(4)	−1 458(2)	2 748(5)	1 902(2)
P(1)	−2 419(2)	43(4)	−501(2)
P(2)	−668(2)	1 507(4)	2 376(2)
O(1)	−2 468(5)	103(10)	−1 457(5)
O(2)	−2 961(5)	−1 220(11)	−398(6)
O(3)	−305(4)	2 683(12)	3 051(6)
O(4)	−853(5)	115(13)	2 949(6)
N(1)	−988(5)	3 170(13)	−162(7)
C(1)	−590(7)	2 544(18)	−613(10)
C(2)	−260(8)	3 290(19)	−1 127(10)
C(3)	−327(8)	4 936(23)	−1 184(10)
C(4)	−743(8)	5 680(18)	727(11)
C(5)	−1 068(7)	4 778(17)	−239(10)
C(11)	−2 433(8)	−1 345(21)	−1 977(10)
C(12)	−1 887(10)	−1 189(26)	−2 410(12)
C(13)	−3 067(10)	−1 487(22)	−2 544(12)
C(21)	−3 055(9)	−1 771(24)	418(12)
C(22)	−3 585(15)	−1 163(39)	645(19)
C(23)	−3 075(28)	−3 413(46)	357(38)
C(31)	344(8)	2 371(24)	3 474(12)
C(32)	690(12)	3 810(32)	3 529(15)
C(33)	336(13)	1 628(42)	4 278(19)
C(41)	−1 106(11)	−1 434(19)	2 605(12)
C(42)	−1 765(12)	−1 599(27)	2 774(18)
C(43)	−664(13)	−2 663(25)	3 024(15)

Table 5. Molecular dimensions (distances in Å, angles in °) in the co-ordination spheres of complexes (**1**) and (**2**)

Complex (**1**)			
S(1)–Zn	2.292(5)	N(1)–Zn	2.077(13)
S(3)–Zn	2.331(5)	N(2)–Zn	1.922(16)
S(3)–Zn–S(1)	108.43(18)	N(1)–Zn–S(3)	107.55(49)
N(1)–Zn–S(1)	114.91(38)	N(2)–Zn–S(3)	120.67(43)
N(2)–Zn–S(1)	117.23(45)	N(2)–Zn–N(1)	86.0(6)
Complex (**2**)			
S(1)–Zn	2.502(4)	S(4)–Zn	2.269(4)
S(2)–Zn	2.358(4)	N(1)–Zn	2.015(12)
S(3)–Zn	3.032(4)		
S(2)–Zn–S(1)	84.87(13)	S(4)–Zn–S(2)	128.91(17)
S(3)–Zn–S(1)	169.29(13)	N(1)–Zn–S(2)	109.13(34)
S(4)–Zn–S(1)	103.97(15)	S(4)–Zn–S(3)	75.81(13)
N(1)–Zn–S(1)	100.70(31)	N(1)–Zn–S(3)	88.60(30)
S(3)–Zn–S(2)	87.08(13)	N(1)–Zn–S(4)	117.96(33)

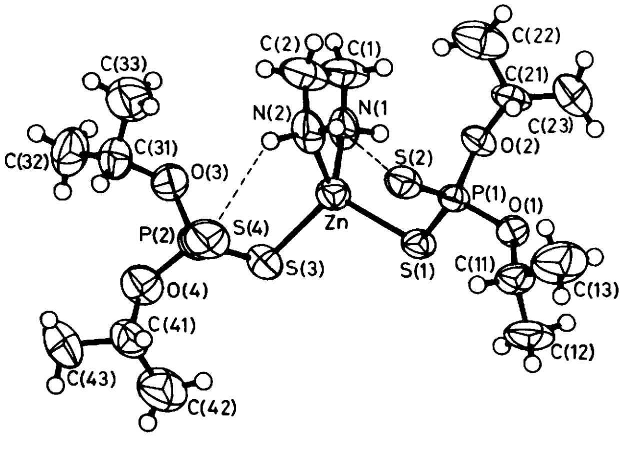

Figure 1. The structure of $[Zn\{S_2P(OPr^i)_2\}_2]$·en (**1**) with the atomic numbering system. Intramolecular hydrogen bonds are shown as dotted lines

sulphur atoms of monodentate dithiophosphate ligands. The geometry of the co-ordination sphere is a severely distorted tetrahedron. The plane formed by Zn,S(1),S(3) intersects the plane of Zn,N(1),N(2) at 87.7° (which is close to the 90° expected for a regular tetrahedron), but whereas the two sulphur atoms are symmetrically arranged on either side of the Zn,N(1),N(2) plane [S(1) −1.80, S(2) 1.88 Å] the nitrogen atoms are asymmetrically disposed with respect to the Zn,S(1),S(3) plane [N(1) 1.70, N(2), −1.14 Å]. The reasons for this gross distortion are not obvious but it is concomitant with significant differences in the zinc–nitrogen distances [Zn–N(1) 2.077(13), Zn–N(2) 1.922(16) Å]. The shorter distance is comparable to the distances observed[9] in $[Zn(en)_2I]_2[C_2O_4]$ (1.843 and 1.968 Å) while the longer distance is within the range (2.05—2.30 Å) more commonly observed.[9–12] Considering the angles subtended at the metal, the 'bite' of the en ligand will obviously account for the small N(1)–Zn–N(2) angle [86.0(6)°]. Of the remainder, it is interesting that angles involving N(2), the

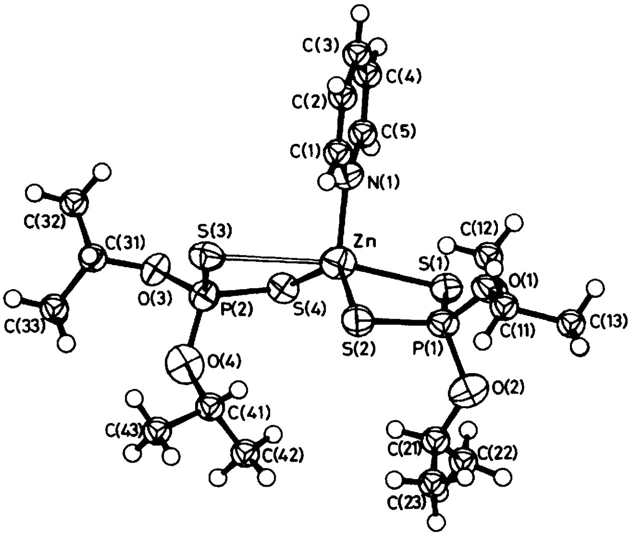

Figure 2. The structure of $[Zn\{S_2P(OPr^i)_2\}_2]$·py (**2**) with the atomic numbering scheme. The long Zn–S(3) bond is shown unshaded

most strongly bound nitrogen atom, are greater than the others. This effect can be observed by a comparison of N(2)–Zn–S(1) [117.2(5)°] and N(2)–Zn–S(3) [120.7(4)°] with S(1)–Zn–S(3) [108.4(2)°], N(1)–Zn–S(1) [114.9(4)°], and N(1)–Zn–S(3) [107.6(5)°].

One possible reason for the observed distortions is the formation of weak hydrogen bonds between the unco-ordinating sulphur atoms S(2) and S(4) and the amino-hydrogen atoms. There are two intramolecular hydrogen bonds involving N(2), namely between N(2)–HN(21) and S(2) [N(2) $\cdots$ S(2) 3.40(2) Å, N(2)–HN(21) $\cdots$ S(2) 146(2)°, HN(21) $\cdots$ S(2) 2.57(2) Å] and between N(2)–HN(22) and S(4) [N(2) $\cdots$ S(4) 3.48(2) Å, N(2)–HN(22) $\cdots$ S(4) 138(2)°, HN(22) $\cdots$ S(4) 2.71(2) Å] and one intermolecular hydrogen bond between N(1)–HN(11) and $S(4^I)$ [symmetry element I $x,\frac{1}{2} - y,\frac{1}{2} + z$: N(1) $\cdots$ $S(4^I)$ 3.48(2) Å, N(1)–HN(11) $\cdots$ $S(4^I)$ 155(2)°, HN(11) $\cdots$ $S(4^I)$ 2.60(2) Å]. These contacts are within the expected range for H $\cdots$ S hydrogen bonds and the relative geometry of contributing atoms is compatible with similar interactions previously documented. The intramolecular hydrogen bonds are shown in Figure 1.

The anions $[S_2P(OPr^i)_2]^-$ are monodentate. The bonded zinc–sulphur distances [S(1) 2.292(5), S(3) 2.331(5) Å] are similar to the distances[5] formed by the monodentate anions in $[Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]^-$ [2.308(4) and 2.296(4) Å]. The difference between the two zinc–sulphur distances observed in the present structure is significant and is reflected in the related phosphorus–sulphur distances [P(1)–S(1) 2.003(6), P(2)–S(3) 1.974(6) Å].

There are two factors that may prohibit the formation of chelating dithiophosphate ligands in this structure. First the formation of hydrogen bonds to the amine nitrogen atoms and secondly the overall crowding of the co-ordination sphere by the bulky ligands.

In complex (**2**) the metal atom is best considered as five-co-ordinate with an approximate trigonal-bipyramidal geometry. The Zn–N distance [2.015(12) Å] is typical of a neutral nitrogen donor bonded to zinc whereas the Zn–S distances are very disparate. That to S(2) [2.358(4) Å] is typical of zinc dialkyl dithiophosphate complexes whereas the Zn–S(4) bond [2.269(4) Å] is the shortest yet recorded in this type of complex. The Zn–S(1) and Zn–S(3) distances [2.502(4) and 3.032(4) Å respectively] are both longer than those usually found. Indeed the Zn–S(3) distance lies midway between usual values and the estimated van der Waals contact distance for zinc and sulphur (3.75 Å).

If we ignore the interaction between the zinc atom and S(3) (*i.e.* treating the species as being four-co-ordinate) the angles subtended at the metal cover the range 84.9(1)—128.9(2)°, a larger distortion from tetrahedral geometry than observed in complex (**1**) [*viz.* 86.0(6)—120.7(4)°]. In approximate trigonal bipyramidal geometry S(1) and S(3) occupy the axial sites [S(1)–Zn–S(3) 169.29(13)°] and S(4), N(1), and S(2) the trigonal plane [angles in the plane S(4)–Zn–N(1) 118.0(3), S(4)–Zn–S(2) 129.0(2), and N(1)–Zn–S(2) 109.1(3)°]. The zinc atom is displaced from the trigonal plane by 0.25 Å towards S(1). Thus the repulsive interactions between axial and equatorial donor atoms are approximately equivalent with S(1) and S(3) being −2.71 and 2.75 Å from the equatorial plane respectively. With the exception of S(1)–Zn–S(2) [84.9(1)°] which is influenced by the ligand bite, the angles subtended at zinc by S(1) and the equatorial atoms are greater than 90° [100.7(3) and 104.0(2)°] and those involving S(3) are less than 90° [75.8(1), 87.1(1), and 88.6(3)°].

For all of the published $[Zn\{S_2P(OR)_2\}_2]$ structures we have calculated both the deviation of the metal atom from the PS_2 planes, ΔM, and the difference in the P–S bond lengths, Δ(P–S), for each PS_2 moiety. For bidentate $[(RO)_2PS_2]^-$, ΔM lies between 0.08 and 0.41 Å and Δ(P–S) between 0.009 and 0.024 Å, whereas for the monodentate ligands the corresponding ranges are 0.97—1.78 and 0.06—0.09 Å. For the P(2),S(3),S(4) fragment in complex (**2**) ΔM is 0.69 Å and Δ(P–S) 0.072 Å suggesting that the bonding of this group is intermediate between mono- and bi-dentate.

The structure of complex (**2**) contrasts with that of $[Zn(S_2CNMe_2)_2]$·py where the zinc atom is unambiguously five-co-ordinate,[13] being bonded to four sulphur atoms [Zn–S range 2.325(4)—2.612(4) Å] and the pyridine nitrogen atom [Zn–N 2.079(6) Å]. The reason for the difference between the two structures is probably steric in nature as the dimethyldithiocarbamate residues are planar and thus require less space than the bulkier $[S_2P(OPr^i)_2]^-$ moieties.

Reaction of $[Zn\{S_2P(OR)_2\}_2]$ (R = Et *or* Pr^i) *with* en, dmen, *and* tmen.—The nature of the products from the reactions of $[Zn\{S_2P(OPr^i)_2\}_2]$ or $[Zn\{S_2P(OEt)_2\}_2]$ with en, dmen (*NN′*-dimethylethylenediamine), and tmen (*NNN′N′*-tetramethylethylenediamine) is a function of the stoicheiometry of the reactants and the steric requirements of the ligand. Thus with en two products were isolated, namely $[Zn\{S_2P(OR)_2\}_2]$·en and $[Zn(en)_3][S_2P(OR)_2]_2$; the former was obtained when $[Zn\{S_2P(OR)_2\}_2]$ and en were allowed to react in a 1:1 molar ratio and the latter when the molar ratio was 1:3. The ^{31}P n.m.r. spectra of solutions in which the $[Zn\{S_2P(OPr^i)_2\}_2]$: en ratio was increased from 1:1 to 1:3 did not exhibit the resonance characteristic of ionic $[S_2P(OPr^i)_2]^-$ (see later) until the molar ratio reached 1:3, thus suggesting that $[Zn(en)_2][S_2P(OR)_2]_2$ is not formed.

On treating $[Zn\{S_2P(OR)_2\}_2]$ with dmen two species were obtained, namely the 1:1 adduct and the ionic species $[Zn(dmen)_2][S_2P(OR)_2]_2$. The choice of molar ratio determined which product was obtained and ^{31}P n.m.r. studies (Table 6) on $[Zn\{S_2P(OR)_2\}_2]$–dmen mixtures revealed that when the molar ratio reached 1:2 ionic $[S_2P(OR)_2]^-$ was formed. With the largest ligand, tmen, only one product was isolated, *viz.* $[Zn\{S_2P(OR)_2\}_2]$·tmen. The ^{31}P n.m.r. spectra of solutions formed by the addition of an excess of tmen to $[Zn\{S_2P(OR)_2\}_2]$·tmen contained no evidence for the formation of ionic $[S_2P(OR)_2]^-$. As similar results were obtained with R = Et and R = Pr^i (see Table 6) the nature of the products seems to be

Table 6. ^{31}P N.m.r. spectral data for $[Zn\{S_2P(OR)_2\}_2]$·nitrogen base complexes and other dialkyl dithiophosphate (R = Et or Pr^i) species[a]

Group	Compound	$\delta(^{31}P)^b$/p.p.m.	Compound	$\delta(^{31}P)^b$/p.p.m.
A	$[NH_4][S_2P(OPr^i)_2]$	*107.4	$[NH_4][S_2P(OEt)_2]$	*110.9
	$[Zn(en)_3][S_2P(OPr^i)_2]_2$	105.4, *107.4	$[Zn(en)_3][S_2P(OEt)_2]_2$	108.2, *110.8
	$[Zn(dmen)_2][S_2P(OPr^i)_2]_2$	104.2, *107.4		
B	$[Zn\{S_2P(OPr^i)_2\}_2]$·en	101.1	$[Zn\{S_2P(OEt)_2\}_2]$·en	104.0
	$[Zn\{S_2P(OPr^i)_2\}_2]$·dmphen	100.2	$[Zn\{S_2P(OEt)_2\}_2]$·dmen	103.9
	$[Zn\{S_2P(OPr^i)_2\}_2]$·phen	99.9	$[Zn\{S_2P(OEt)_2\}_2]$·dmphen	102.8
	$[Zn\{S_2P(OPr^i)_2\}_2]$·bipy	99.8	$[Zn\{S_2P(OEt)_2\}_2]$·bipy	102.8
	$[Zn\{S_2P(OPr^i)_2\}_2]$·tmen	99.0	$[Zn\{S_2P(OEt)_2\}_2]$·phen	102.6
			$[Zn\{S_2P(OEt)_2\}_2]$·tmen	101.6
C	$[Zn\{S_2P(OPr^i)_2\}_2]$·py	96.9	$[Zn\{S_2P(OEt)_2\}_2]$·py	100.3
D	$[Zn\{S_2P(OPr^i)_2\}_2]$	94.2	$[Zn\{S_2P(OEt)_2\}_2]$	98.2

[a] In deuteriochloroform except those marked with an asterisk, which are in D_2O or water. [b] Relative to 85.5% H_3PO_4, positive values downfield.

a function of the nitrogen base and not of the steric requirements of the anion. The results with these simple ligands suggest that in the presence of an excess of aliphatic chelating nitrogen ligand (containing either primary or secondary nitrogen atoms) ionic $[S_2P(OR)_2]^-$ is formed from $[Zn\{S_2P(OR)_2\}_2]$.

Reaction of $[Zn\{S_2P(OR)_2\}_2]$ (R = Et *or* Pr^i) *with Aromatic Nitrogen Bases.*—Both 1:1 and 1:2 adducts of $[Zn\{S_2P(OR)_2\}_2]$ with pyridine have been reported.[4,5] We investigated the reaction of $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i) with pyridine with particular emphasis being placed upon the Pr^i complex. Using Zn:py ratios between 2:1 and 1:8 we obtained only the 1:1 adduct. The only variation with change in molar ratio was in the time taken for precipitation to occur, which ranged from 20 min (molar ratio 1:2) to 7 d (molar ratio 1:8). Identical results were obtained with R = Et. However only a 1:2 adduct was obtained when $[Zn_4O\{S_2P(OPh)_2\}_6]$ was treated with pyridine (see later).

Our failure to isolate 1:2 complexes with R = Et or Pr^i is surprising, although a report of the 1:2 compounds states that the products are 'sticky' and subject to loss of pyridine when stored at room temperature.[4] The ^{31}P n.m.r. spectra of the 1:1 pyridine adducts for R = Et and Pr^i have resonances at 100.3 and 96.9 p.p.m. respectively, while the resonances of compounds in which there are known to be two nitrogen atoms bound to the metal are in the region 101.6—104.0 p.p.m. for R = Et and 99.0—101.1 p.p.m. for R = Pr^i (Table 6). Studies of the change of position of the ^{31}P resonance with increasing pyridine concentration revealed that for R = Pr^i the resonance did shift to higher p.p.m. with increase in pyridine concentration and in neat pyridine reached a value (99.7 p.p.m.) in the range expected for a species in which two nitrogen atoms are bound to the metal. Such a shift may be evidence for the formation of a 1:2 compound in solution; it was from a solution in neat pyridine that the 1:2 compound was isolated. Alternatively the shift may be interpreted as a solvent effect. The Gibbs free energy for the formation of the 1:2 pyridine adducts[4] from the 1:1 adduct has been determined as -7 kJ mol^{-1}, which corresponds to an equilibrium constant of approximately 17 dm^3 mol^{-1}, and so the transformation of the 1:2 to the 1:1 adduct could be relatively easily achieved by reduction in the pyridine concentration.

In contrast to the behaviour of pyridine, addition of the bidentate chelating donors 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and 2,9-dimethyl-1,10-phenanthroline (dmphen) to solutions of $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i) led to the formation of complexes in which two nitrogen atoms were co-ordinated to the metal atom, thus reflecting the power of the chelate effect.

^{31}P *N.M.R. Studies.*—In an attempt to obtain a method for readily detecting the mode of bonding of $[S_2P(OR)_2]^-$ in engine oils, we have measured the positions of the ^{31}P resonances for $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i) and a range of adducts (Table 6). All the compounds examined show a single sharp resonance, and there is approximately 3 p.p.m. between the resonances of the analogous ethyl and isopropyl compounds, those of the ethyl being at lower field. These observations are in accord with a previous study.[5] A related study of binary dialkyl dithiophosphates has been reported.[14]

The spectra can be divided into a number of groups. Group A in Table 6 consists of known ionic species and species believed to be ionic. The compounds $[Zn(en)_3][S_2P(OR)_2]_2$ (R = Et or Pr^i) and $[Zn(dmen)_2][S_2P(OPr^i)_2]_2$ were examined in D_2O to compare the resonances with those of $[NH_4][S_2P(OR)_2]$, a compound known to be ionic, and in $CDCl_3$, to provide a reference for ionic compounds in $CDCl_3$.

The ^{31}P n.m.r. spectrum of complex (**1**) has a ^{31}P resonance at 101.1 p.p.m. Resonances in a similar position (Group B) are shown by $[Zn\{S_2P(OPr^i)_2\}_2]$·L (L = bipy, phen, dmphen, or tmen) and thus it is suggested that the range of 99.0—101.1 p.p.m. is characteristic for unidentate $[S_2P(OPr^i)_2]^-$. For R = Et the range is 101.6—104 p.p.m.

The compounds $[Zn\{S_2P(OR)_2\}_2]$ (R = Et or Pr^i) (Group D) have been shown to be monomeric in dilute solution,[4] hence values are obtained for compounds containing only chelating $[S_2P(OR)_2]^-$ groups.

The chemical shift for $[Zn\{S_2P(OR)_2\}_2]$·py (R = Et or Pr^i) (Group C) lies almost midway between the typical values for monodentate (Group B) and bidentate $[S_2P(OR)_2]^-$ ligands (Group D). Thus for R = Pr^i the mean is 97.1 p.p.m. (observed value 96.9) while for R = Et it is 100.6 p.p.m. (observed value 100.3 p.p.m.). The bonding situation in complex (**2**) (R = Pr^i) is rather more complicated than a monodentate and a bidentate ligand as there is an additional weak Zn–S(3) bond. Presumably there is a rapid interchange between the quasi-monodentate and bidentate bonding modes which lead to one resonance for Group C molecules being observed even at -90 °C in CD_2Cl_2 solution. We have demonstrated that it is possible to predict the 'average' mode of bonding of $[S_2P(OR)_2]^-$ groups by the use of ^{31}P n.m.r. spectroscopy which should prove useful in ascertaining whether in engine oils containing $[Zn\{S_2P(OR)_2\}_2]$–amine mixtures the zinc is actually bound to the $[S_2P(OR)_2]^-$ groups.

'Basic' Zinc Dialkyl Dithiophosphates.—The partial crystal structure of the 'basic' butyl compound has been published and the results are suggested to indicate that the compound exists as $[Zn_4O\{S_2P(OR)_2\}_6]$ molecules.[15] We have made three of the 'basic' salts with R = Pr^i, Bu, and Ph. The compound with R = Pr^i gave crystals that were unsuitable while with R = Bu

crystals that were isomorphous with the crystals previously studied were isolated [rhombohedral, space group $R3$ or $R\bar{3}$, $a = 14.58(1)$ Å, $\alpha = 112.1(1)^\circ$, $Z = 1$]. We measured intensity data but were unable to solve the structure because of disorder and came to the same conclusion as the previous workers. The 'basic' compound with R = Ph gave cubic crystals, space group $Fd3c$ or $Fd3m$, $a = 32.25(2)$ Å, $Z = 16$. We measured intensity data but were unable to solve the structure because of a similar disorder to that observed with R = Bu. However we can conclude that it is highly probable that both compounds contain the Zn_4O core as has been established for $[Zn_4O(O_2CMe)_6]$ and $[Zn_4O(BO_3)_6]$.[16,17]

The 'basic' compounds have characteristic absorptions in their i.r. spectra in the region 470—500 cm^{-1} not shown by the $[Zn\{S_2P(OR)_2\}_2]$ compounds and these diagnostic bands we associate with the Zn_4O tetrahedron. In addition to the unique i.r. absorptions the 'basic' compounds exhibit more complicated ^1H n.m.r. spectra than their related $[Zn\{S_2P(OR)_2\}_2]$ species. Thus for R = Pr^i ($CDCl_3$ solution, 60 MHz) there is a resonance at 1.40 p.p.m. characteristic of $[Zn\{S_2P(OPr^i)_2\}_2]$, and a more intense resonance at 1.36 p.p.m. which we attribute to the 'basic' compound. A sample of $[Zn_4O\{S_2P(OPr^i)_2\}_6]$ was dissolved in $CDCl_3$ and its ^1H n.m.r. spectrum measured immediately and after 4 d. The initial spectrum gave a ratio of $[Zn\{S_2P(OPr^i)_2\}_2]$ to basic compound of 1:5 while after 4 d it had become 1:2. However, if the final solution was taken and the solvent removed by evaporation and the resulting solid dissolved in fresh solvent the ratio 1:5 was obtained indicating that there is a dynamic equilibrium between the basic compounds and their related $[Zn\{S_2P(OR)_2\}_2]$ species. Similar effects were observed with a range of R groups and in a variety of solvents.

We allowed $[Zn_4O\{S_2P(OR)_2\}_6]$ to react with a number of amines to ascertain whether the 'basic' structure was ruptured by the ligands. Initially $[Zn_4O\{S_2P(OPr^i)_2\}_6]$ was treated with rigorously dried tmen under air- and moisture-free conditions. A white precipitate was obtained which was shown by zinc determinations and *X*-ray powder photography to be ZnO, the other product being $[Zn\{S_2P(OPr^i)_2\}_2]\cdot$tmen. The isolation of ZnO rather than some hydroxo species tends to support the structure of the basic compound as $[Zn_4O\{S_2P(OR)_2\}_6]$.

In addition to the reaction of tmen, reactions of en, dmen, py, and bipy with $[Zn_4O\{S_2P(OR)_2\}_6]$ (R = Pr^i or Ph) were carried out and the products were equivalent to those obtained from $[Zn\{S_2P(OR)_2\}_2]$ (see earlier). However the reaction of $[Zn_4O\{S_2P(OPh)_2\}_6]$ with pyridine gave a 1:2 adduct. This result contrasts with that obtained with R = Pr^i (1:1 adduct) and perhaps reflects the ease with which planar Ph rings are able to pack compared to bulky Pr^i groups. We conclude that if the basic compound is formed as an oxidation product in engine oil it is unlikely to persist as an independent moiety as it will react with amines in the oil.

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