# Zinc(II) Bis(*O,O'*-dialkyl dithiophosphates): Interaction with Small Nitrogen Bases. The Crystal and Molecular Structure of Hexakis($\mu$-*O,O'*-diethyl dithiophosphato)-$\mu_4$-thio-tetrazinc, $Zn_4[S_2P(OEt)_2]_6S$†

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In the presence of atmospheric moisture, triethylamine, diethylamine, and 1,5-diazabicyclo[4.3.0]non-5-ene promote the hydrolysis of zinc(II) bis(*O,O'*-dialkyl dithiophosphates), $Zn[S_2P(OR)_2]_2$ (R = Et or Pr$^i$), to the corresponding hexakis(*O,O'*-dialkyl dithiophosphato)-$\mu_4$-oxo-tetrazinc derivatives, $Zn_4[S_2P(OR)_2]_6O$. Under anhydrous conditions, however, the complexes $Zn[S_2P(OEt)_2]_2 \cdot 2.75NHEt_2$ and $Zn[S_2P(OPr^i)_2]_2 \cdot nNEt_3$ ($n$ = 1 or 2.75) are obtained. The crystal and molecular structure of hexakis(*O,O'*-diethyl dithiophosphato)-$\mu_4$-thio-tetrazinc, $Zn_4[S_2P(OEt)_2]_6S$, a by-product in the synthesis of $Zn[S_2P(OEt)_2]_2$, is also reported. Crystals are trigonal, space group *R*3 (no. 146), with $a$ = 20.776(2), $c$ = 11.560(2) Å, and $Z$ = 3. The structure determination was carried out by the heavy-atom method using Mo-$K_\alpha$ radiation ($\lambda$ = 0.7107 Å) from 1 455 independent reflections with $I > 3\sigma(I)$. The structure comprises independent, non-interacting molecules of composition $Zn_4[S_2P(OEt)_2]_6S$, which possess crystallographically-imposed three-fold symmetry. The three-fold axis is collinear with the unique Zn–S bond of the central $Zn_4S$ core, which possesses nearly perfect tetrahedral symmetry [Zn–S 2.264(6) Å, 2.267(2) Å]. Each of the zinc–zinc axes of the tetrahedron is bridged almost symmetrically by the dithiophosphate ligands at somewhat longer zinc–sulphur distances [ligand 1, 2.341(4), 2.353(4); ligand 2, 2.335(3), 2.337(3) Å].

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Zinc(II) bis(*O,O'*-dialkyl dithiophosphates),‡ $Zn[S_2P(OR)_2]_2$ (R generally a long alkyl group), have been key additives to motor vehicle lubricating oils for over 40 years because of their high antioxidant activity and antiwear properties. The efficacy with which $Zn[S_2P(OR)_2]_2$ performs these functions is known to be dependent on the nature of the particular derivative employed, and also upon the composition of the overall engine oil additive package. In particular, both detergent (*e.g.*, sodium or alkaline earth sulphates, phenates, phosphonates, and salicylates) and dispersant (*e.g.*, succinimide derivatives of amines and polyether polyalcohols) additives, as well as their degradation products (*e.g.*, amines, peroxides, *etc.*) play a major role in the effectiveness of $Zn[S_2P(OR)_2]_2$. Whilst the mode of operation of $Zn[S_2P(OR)_2]_2$ as antiwear agents is largely unknown (although chemisorption of some dithiophosphate species on the metal surface is most probably involved[1]), it has long been known that $Zn[S_2P(OR)_2]_2$ compounds are effective scavengers of organic peroxides. The most recent data, however, suggest that it is the free *O,O'*-dialkyl dithiophosphoric acids, $(RO)_2PS_2H$, derived *in situ*, which actually catalyse the decomposition of hydroperoxides, a process which is also promoted by the disulphides, $[(RO)_2PS_2]_2$.[2] Several studies[3–8] have shown that disulphides are formed in the reaction of $Zn[S_2P(OR)_2]_2$ with hydroperoxides along with the so-called 'basic' zinc *O,O'*-dialkyl dithiophosphates of composition $Zn_4[S_2P(OR)_2]_6O$.[9] These latter compounds are inactive as antioxidants and antiwear agents and are, therefore, undesirable but can be present in the original $Zn[S_2P(OR)_2]_2$ additive mix as a result of the manufacturing process. Since most of the attention in this area has been focused on the interaction of $Zn[S_2P(OR)_2]_2$ with peroxides, we have endeavoured to elucidate the effect of the several other types of materials present on zinc *O,O'*-dialkyl dithiophosphate constitution in solution and their activity. In this and subsequent papers, we describe our studies of the various zinc *O,O'*-dialkyl dithiophosphate species which are formed by the interaction of $Zn[S_2P(OR)_2]_2$ with other molecules.

## Experimental

*Synthetic procedures.*—Syntheses of authentic samples of $Zn[S_2P(OR)_2]_2$ (R = Et or Pr$^i$) were a modification of literature procedures.[10,11]

*Synthesis of bis(*O,O'*-diethyl dithiophosphato)zinc(*II*) and hexakis(*$\mu$-O,O'*-diethyl dithiophosphato)-*$\mu_4$*-thio-tetrazinc(*II*).* Zinc oxide (39.90 g, 0.4904 mol) was slowly added to a brown-black solution of *O,O'*-diethyl dithiophosphoric acid [from the reaction of ethanol (1.6809 mol) and diphosphorus(V) pentasulphide (64.20 g, 0.2889 mol) under ethanol-saturated nitrogen] yielding a white slurry in a very exothermic reaction. The majority of the white precipitate was dissolved in hot ethanol, and the remainder filtered off. From the filtrate was recovered $Zn[S_2P(OEt)_2]_2$ (45.82 g 21.0%), m.p. 81—82 °C (lit.,[12] 77—79 °C) (Found: C, 21.8; H, 4.70. $C_8H_{20}O_4P_2S_4Zn$ requires C, 22.05; H, 4.65%). Recrystallisation of the insoluble material from hot ethanol–dichloromethane (1 : 1 v/v) yielded colourless crystals of $Zn_4[S_2P(OEt)_2]_6S$ (1.44 g, 0.8%), m.p. 202—203 °C (Found: C, 20.4; H, 4.40; S, 30.7. $C_{24}H_{60}O_{12}P_6S_{13}Zn_4$ requires C, 20.5; H, 4.30; S, 29.65%); *cf.* data for $Zn_4[S_2P(OEt)_2]_6O$, which requires C, 20.75; H, 4.35; S, 27.7%. A mixed melting point determination of $Zn_4[S_2P(OEt)_2]_6S$ with $Zn_4[S_2P(OEt)_2]_6O$ (m.p. 195—198 °C) (*ca.* 1 : 1) depressed the melting point to 192—195 °C.

*Synthesis of bis(*O,O'*-di-isopropyl dithiophosphato)zinc(*II*) and hexakis(*$\mu$-O,O'*-di-isopropyl dithiophosphato)*$\mu_4$*-oxo-tetra-*

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† *Supplementary data available* (No. SUP 56460, 5 pp.): i.r. spectra of $Zn_4[S_2P(OEt)_2]_6O$ and $Zn_4[S_2P(OEt)_2]_6S$, thermal parameters, packing diagram. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

‡ These compounds are also known variously as 'zinc bis(dialkyl dithiophosphoridates)' and 'zinc bis(dialkyl phosphorodithioates).'

*zinc*(II). Using a similar procedure, zinc oxide (23.34 g, 0.2868 mol) was added to the brown-black solution of *O,O'*-diisopropyl dithiophosphoric acid [from the reaction of isopropyl alcohol (1.306 mol) and $P_2S_5$ (64.09 g, 0.2884 mol) over a period of 2 h], and the mixture stirred for 1 h after the initial exothermic reaction had subsided. The products from this reaction were $Zn[S_2P(OPr^i)_2]_2$ (42.12 g, 30.0%), m.p. 140—142 °C (lit.,[12] 141—142 °C) (Found: C, 29.5; H, 5.90. $C_{12}H_{28}O_4P_2S_4Zn$ requires C, 29.3; H, 5.75%), $Zn_4[S_2P(OPr^i)_2]_6O$ (0.12 g, 0.1%), m.p. 198—200 °C (Found: C, 27.7; H, 5.75. $C_{36}H_{84}O_{13}P_6S_{12}Zn_4$ requires C, 27.75; H, 5.45%), $[(Pr^iO)_2PS_2]_2$ m.p. 84—88 °C (lit.,[13] 91 °C) (Found, C, 32.15; H, 6.50. $C_{12}H_{28}O_4P_2S_4$ requires C, 33.8; H, 6.60%), and elemental sulphur (0.3 g).

*Interaction of Zinc*(II) *Bis*(O,O'*-dialkyl dithiophosphates*) *with Triethylamine, Diethylamine, and* 1,5-*Diazabicyclo*[4.3.0]*non-5-ene*.—(*a*) The addition of triethylamine or diethylamine (0.0004 mol) to a solution of $Zn[S_2P(OR)_2]_2$ (R = Et or $Pr^i$) (0.0004 mol) in carbon tetrachloride (4 $cm^3$) resulted in the slow precipitation of the appropriate $Zn_4[S_2P(OR)_2]_6O$ derivative. R = Et (0.04 g, 29.0%), m.p. 198—200 °C (Found: C, 20.7; H, 4.40; S, 27.3. $C_{24}H_{60}O_{13}P_6S_{12}Zn_4$ requires C, 20.75; H, 4.35; S, 27.7%). R = $Pr^i$ (0.05 g, 32.1%), m.p. 200 °C (Found: C, 27.8; H, 5.50; S, 25.05. $C_{36}H_{84}O_{13}P_6S_{12}Zn_4$ requires C, 27.75; H, 5.45; S, 24.1%).

(*b*) The same $Zn_4[S_2P(OR)_2]_6O$ products were also obtained when 1,5-diazabicyclo[4.3.0]non-5-ene (dabn) (0.012 $cm^3$, 0.0001 mol) was added to a solution of $Zn[S_2P(OR)_2]_2$ (0.0004 mol) in carbon tetrachloride (4 $cm^3$), and the solution allowed to stand overnight. R = Et (Found: C, 20.9; H, 4.25; S, 28.55%). R = $Pr^i$ (Found: C, 27.4; H, 5.35%).

(*c*) Employing toluene as the solvent in (*a*) or (*b*) with $Zn[S_2P(OEt)_2]_2$ afforded white crystals of a toluene solvate of $Zn_4[S_2P(OEt)_2]_6O$, m.p. 208—210 °C (Found: C, 21.9, 21.65; H, 4.40, 4.45; S, 28.35, 26.6. $C_{24}H_{60}O_{13}P_6S_{12}Zn{\cdot}0.2C_7H_8$ requires C, 21.7; H, 4.40; S, 27.35%).

(*d*) Triethylamine (4 $cm^3$, 0.029 mol) was added to $Zn[S_2P(OPr^i)_2]_2$ (14.524 g, 0.030 mol) dissolved in carbon tetrachloride (30 $cm^3$). A white precipitate began to form immediately, and after 2 h $Zn_4[S_2P(OPr^i)_2]_6O$ (4.68 g, 40.2%), m.p. 198—200 °C, was obtained as a white powder (Found: C, 28.2; H, 5.60%). On allowing to stand the filtrate became yellow, and deposited white crystals of the triethylamine complex, $Zn[S_2P(OPr^i)_2]_2{\cdot}1.5NEt_3$ (2.33 g, 12.3%), m.p. 85 °C (Found: C, 39.35; H, 8.40; N, 3.05. $C_{12}H_{28}O_4P_2S_4Zn{\cdot}1.5C_6H_{15}N$ requires C, 39.1; H, 7.90; N, 3.25%).

(*e*) Diethylamine (0.084 $cm^3$, 0.0008 mol) and $Zn[S_2P(OEt)_2]_2$ (0.1854 g, 0.0004 mol) were refluxed for 1 h in carbon tetrachloride (10 $cm^3$). After *ca.* 5 min the solution became yellow and eventually brown. On standing, white crystals of the complex, $Zn[S_2P(OEt)_2]_2{\cdot}2.75NHEt_2$, were obtained (Found: C, 36.15; H, 8.30; N, 5.90. $C_8H_{20}O_4P_2S_4Zn{\cdot}2.75C_4H_{11}N$ requires C, 33.75; H, 7.95; N, 6.05%).

(*f*) In a procedure similar to (*e*), $Zn[S_2P(OPr^i)_2]_2$ (0.1934 g, 0.0004 mol) and triethylamine (0.102 $cm^3$, 0.0007 mol) were refluxed for 1 h in carbon tetrachloride (10 $cm^3$) affording the complex $Zn[S_2P(OPr^i)_2]_2{\cdot}NEt_3$ as a white solid (Found: C, 36.7; H, 7.65; N, 2.60. $C_{12}H_{28}O_4P_2S_4Zn{\cdot}C_6H_{15}N$ requires C, 36.45; H, 7.30; N, 2.35%).

(*g*) $Zn[S_2P(OPr^i)_2]_2$ (0.2065 g, 0.0004 mol) was dissolved in triethylamine (4.0 $cm^3$, 0.0287 mol). The solution rapidly became yellow, and precipitation of a white solid took place over a period of 30 min. Recrystallisation from triethylamine affords white needle crystals of the complex $Zn[S_2P(OPr^i)_2]_2{\cdot}2.75NEt_3$ (0.05 g, 16.4%), m.p. 104—105 °C (Found: C, 44.45; H, 9.65; N, 4.85. $C_{12}H_{28}O_4P_2S_4Zn{\cdot}2.75C_6H_{15}N$ requires C, 44.35; H, 9.05; N, 5.00%).

*Crystal Structure Determination of Hexakis*(μ-*O,O'-diethyl dithiophosphato*)-μ$_4$-*thio-tetrazinc*(II).—Colourless crystals of the compound suitable for intensity data collection were obtained from the preparation of $Zn[S_2P(OEt)_2]_2$ described above.

*Crystal data.* $C_{24}H_{60}O_{12}P_6S_{13}Zn_4$, *M* = 1 404.89, trigonal, space group *R*3 (No. 146) (hexagonal axes), *a* = 20.776(2), *c* = 11.560(2) Å, *U* = 4 321.3(6) Å$^3$, $D_m$ = 1.7 g $cm^{-3}$ (by flotation using hexane–1,2-dibromoethane–hexachlorobuta-1,3-diene), *Z* = 3, $D_c$ = 1.62 g $cm^{-3}$, *F*(000) = 2 154, Mo-$K_\alpha$ radiation (λ = 0.7107 Å), μ(Mo-$K_\alpha$) = 23.52 $cm^{-1}$. Crystal size, 0.4 × 0.1 × 0.1 mm; no. of reflections with $I > 3\sigma(I)$, 1 455.

*Data collection and structure refinement.* The space group and approximate cell dimensions were measured from oscillation and zero- and first-layer Weissenberg photographs. Accurate cell dimensions were obtained by least-squares refinement of 23 reflections.

Intensity data were recorded in the range $0 < \theta < 25$ ° using a Hilger and Watts Y290 four-circle diffractometer. Reflections with $I < 3\sigma(I)$ were considered unobserved, leaving a total of 1 455 reflections. Intensities were corrected for Lorentz and polarisation effects, but not for absorption due to the low μ value.

The positions of the two crystallographically independent zinc atoms were located from a three-dimensional Patterson synthesis, and these were used to phase subsequent Fourier syntheses which revealed the remaining non-hydrogen light atoms. The two atoms lying on the three-fold axis, Zn(1) and S(5), were assigned an occupancy factor of one-third. Full-matrix least-squares refinement with all atoms anisotropic was continued until convergence, when a weighting scheme of the form shown below was applied, where $\chi = F_o/F_o(\max.)$ and

$$w = 1/\{A[0]{\cdot}T[0]'(\chi) + A[1]{\cdot}T[1]'(\chi)\cdots A[\mathrm{np}-1].T[\mathrm{np}-1]'(\chi)\}$$

np = number of parameters; *A*[*I*] are the coefficients of a Chebyshev series in *T*[*I*]′(χ). Four terms in the series were used with values *A*[0] = 22.8, *A*[1] = 12.4, *A*[2] = −11.0, and *A*[3] = −7.3. The final conventional *R* value was 0.0518 (weighted *R*′ = 0.0639). Attempted refinement with an oxygen atom replacing the central sulphur atom [S(5)] resulted in a divergence of the thermal parameters. In contrast, with sulphur the thermal parameters stabilised at acceptable values. The atomic scattering factors used were those for neutral atoms.[14] A correction for anomalous dispersion was applied to the zinc, sulphur, and phosphorus atoms. Calculations were performed using the CRYSTALS suite of programs.[15] Molecular and unit-cell plots were obtained using PLUTO.[16]

Final fractional atomic co-ordinates are listed in Table 1 and intramolecular bond distances and angles are in Table 2. The atomic numbering is illustrated in the Figure.

## Results and Discussion

Triethylamine and diethylamine, as well as the solely Brönsted base 1,5-diazobicyclo[4.3.0]non-5-ene, promote the slow hydrolysis of $Zn[S_2P(OR)_2]_2$ to the corresponding 'basic' $Zn_4[S_2P(OR)_2]_6O$ compounds in the presence of adventitious moisture, equation (1). Such compounds have been isolated

$$4\,Zn[S_2P(OR)_2]_2 + H_2O \xrightarrow{Y} Zn_4[S_2P(OR)_2]_6O + 2YH[S_2P(OR)_2] \quad (1)$$

$R$ = Et or $Pr^i$; Y = base = $NEt_3$, $NHEt_2$, or dabn

previously as by-products from the synthesis of 'normal' $Zn[S_2P(OR)_2]_2$ compounds.[10,17] From a larger scale reaction

**Table 1.** Final fractional atomic co-ordinates with estimated standard deviations in parentheses

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Zn(1) | 0.0000 | 0.0000 | 0.0000 |
| Zn(2) | 0.556 50(7) | 0.316 89(7) | 0.072 5(2) |
| S(1) | 0.568 5(2) | 0.131 2(2) | 0.049 4(4) |
| S(2) | 0.530 8(2) | 0.251 8(2) | −0.102 0(4) |
| S(3) | 0.112 8(2) | 0.200 0(2) | −0.120 4(4) |
| S(4) | 0.122 0(2) | 0.075 5(2) | 0.065 2(4) |
| S(5) | 0.6667 | 0.3333 | 0.137 5(5) |
| P(1) | 0.506 4(2) | 0.148 6(2) | −0.062 4(4) |
| P(2) | 0.156 3(2) | 0.178 4(2) | 0.016 4(4) |
| O(1) | 0.425 5(5) | 0.099 0(5) | −0.008 1(9) |
| O(2) | 0.498 6(5) | 0.107 8(5) | −0.180 0(8) |
| O(3) | 0.157(1) | 0.226 3(8) | 0.117(1) |
| O(4) | 0.241 8(8) | 0.210(1) | 0.004(2) |
| C(1) | 0.360 7(9) | 0.091(1) | −0.072(2) |
| C(2) | 0.295(1) | 0.040(2) | −0.006(2) |
| C(3) | 0.560(1) | 0.131(1) | −0.258(1) |
| C(4) | 0.545(2) | 0.076(1) | −0.348(2) |
| C(5) | 0.098(2) | 0.212(1) | 0.189(3) |
| C(6) | 0.116(2) | 0.258(1) | 0.284(2) |
| C(7) | 0.293(2) | 0.265(3) | −0.037(3) |
| C(8) | 0.361(1) | 0.287(2) | −0.080(3) |

**Table 2.** Interatomic bond distances (Å) and angles (°) with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Zn(1)–Zn(2) | 3.697(2) | Zn(2)–Zn(1)–Zn(2′) | 60.13(5) |
| Zn(1)–S(4) | 2.341(4) | S(4)–Zn(1)–S(4′) | 110.2(1) |
| Zn(1)–S(5) | 2.264(6) | S(4)–Zn(1)–S(5) | 108.8(1) |
| Zn(1)–Zn(2′) | 3.704(2) | Zn(2′)–Zn(2)–Zn(2″) | 60.00(0) |
| Zn(2)–S(1) | 2.335(3) | S(1)–Zn(2)–S(5) | 110.4(1) |
| Zn(2)–S(2) | 2.337(3) | S(1)–Zn(2)–S(2) | 111.8(1) |
| Zn(2)–S(3) | 2.353(4) | S(1)–Zn(2)–S(3) | 109.8(2) |
| Zn(2)–S(5) | 2.267(2) | S(2)–Zn(2)–S(3) | 110.7(1) |
| | | S(2)–Zn(2)–S(5) | 107.1(1) |
| | | S(3)–Zn(2)–S(5) | 106.9(2) |
| | | Zn(1)–S(5)–Zn(2) | 109.4(1) |
| | | Zn(2)–S(5)–Zn(2′) | 109.6(1) |
| S(1)–P(1) | 1.983(5) | Zn(2)–S(1)–P(1) | 109.9(2) |
| S(2)–P(1) | 1.993(5) | Zn(2)–S(2)–P(1) | 106.6(2) |
| S(3)–P(2) | 1.981(6) | Zn(2)–S(3)–P(2) | 106.6(2) |
| S(4)–P(2) | 1.968(6) | Zn(1)–S(4)–P(2) | 108.5(2) |
| P(1)–O(1) | 1.60(1) | S(1)–P(1)–O(1) | 101.4(4) |
| P(1)–O(2) | 1.568(9) | S(1)–P(1)–O(1) | 111.6(4) |
| | | S(1)–P(1)–S(2) | 120.5(2) |
| | | S(2)–P(1)–O(1) | 113.8(4) |
| | | S(2)–P(1)–O(2) | 106.5(4) |
| | | O(1)–P(1)–O(2) | 101.6(5) |
| P(2)–O(3) | 1.53(1) | S(3)–P(2)–O(3) | 108.1(8) |
| P(2)–O(4) | 1.56(2) | S(3)–P(2)–O(4) | 112.7(7) |
| | | S(3)–P(2)–S(4) | 121.1(2) |
| | | S(4)–P(2)–O(3) | 111.9(6) |
| | | S(4)–P(2)–O(4) | 101.2(8) |
| | | O(3)–P(2)–O(4) | 100(1) |
| O(1)–C(1) | 1.47(2) | P(1)–O(1)–C(1) | 119(1) |
| O(2)–C(3) | 1.44(2) | P(1)–O(2)–C(3) | 112.1(9) |
| O(3)–C(5) | 1.37(3) | P(2)–O(3)–C(5) | 127(2) |
| O(4)–C(7) | 1.21(5) | P(2)–O(4)–C(7) | 135(3) |
| C(1)–C(2) | 1.45(3) | O(1)–C(1)–C(2) | 107(2) |
| C(3)–C(4) | 1.45(3) | O(2)–C(3)–C(4) | 112(2) |
| C(5)–C(6) | 1.38(3) | O(3)–C(5)–C(6) | 116(3) |
| C(7)–C(8) | 1.33(4) | O(4)–C(7)–C(8) | 139(5) |

of $Zn[S_2P(OPr^i)_2]_2$ with triethylamine, however, a small quantity of the complex $Zn[S_2P(OPr^i)_2]_2{\cdot}1.5NEt_3$ was also isolated from the filtrate after removal of the 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$. Similar Lewis acid–Lewis base complexes could be obtained under anhydrous conditions by either refluxing the reactants in carbon tetrachloride or recrystallising the $Zn[S_2P(OR)_2]_2$ from triethylamine at room temperature. The stoicheiometry of such complexes is variable, but the stable complexes $Zn[S_2P(OPr^i)_2]_2{\cdot}nNEt_3$ ($n$ = 1 or 2.75) and $Zn[S_2P(OEt)_2]_2{\cdot}2.75NHEt_2$ were isolated reproducibly from different preparations. No structural studies were carried out on these complexes, but it is presumed that they possess similar structural features to the complexes with pyridine, 2,2′-bipyridine, 2,2′:6′,2″-terpyridine and 1,11-diamino-3,6,9-triazaundecane reported in the following paper.[18]

Although the 'basic' *O,O′*-dialkyl dithiophosphate products isolated from preparations of 'normal' $Zn[S_2P(OR)_2]_2$ have always been considered to be hexakis(*O,O′*-dialkyl dithiophosphato)-$\mu_4$-oxo-tetrazinc,[9] the by-product isolated from our large-scale synthesis of $Zn[S_2P(OEt)_2]_2$ was not identical to the product obtained by hydrolysis. In particular, microanalysis showed a higher than expected value for the sulphur content, the melting point was slightly higher and the melting point of a mixture with authentic $Zn_4[S_2P(OEt)_2]_6O$ was depressed by *ca.* 10 °C. The i.r. spectrum, which above 800 $cm^{-1}$ was identical with authentic $Zn_4[S_2P(OEt)_2]_6O$, showed differences in the low-energy region (see SUP 56460). In particular, authentic $Zn_4[S_2P(OEt)_2]_6O$ exhibits a band at 491 $cm^{-1}$ absent in the spectrum of the by-product, whose spectrum contains an additional band at 355 $cm^{-1}$. Because of these anomalies, an *X*-ray crystallographic study of this material was undertaken, which indeed showed it to be not $Zn_4[S_2P(OEt)_2]_6O$, but rather its sulphur analogue, $Zn_4[S_2P(OEt)_2]_6S$.

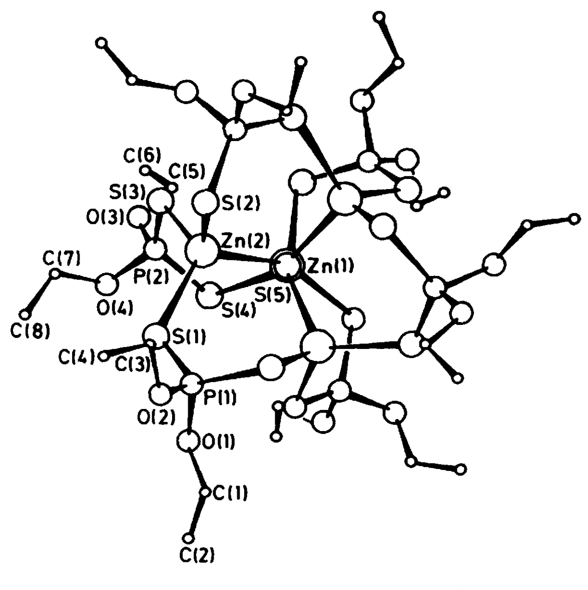

**Figure.** View of $Zn_4[S_2P(OEt)_2]_6S$ along the unique $\bar{3}$ axis

Crystals of the compound comprise independent, non-interacting, discrete molecules of composition $Zn_4[S_2P(OEt)_2]_6S$ (see SUP 56460). Each molecule possesses crystallographically-imposed three-fold symmetry (space group *R*3), the three-fold axis being collinear with the unique zinc–sulphide bond Zn(1)–S(5), of the central $Zn_4S$ unit (Figure). Nevertheless, this unit exhibits almost perfect tetrahedral symmetry [Zn–S 2.264(6), 2.267(2) Å; bond angles at S(5) 109.4(1), 109.6(1)°; Zn(2)–Zn(1)–Zn(2′) 60.13(5), Zn(2′)–Zn(2)–Zn(2″) 60° (by symmetry)]. Each of the zinc–zinc axes is bridged essentially symmetrically by the *O,O′*-diethyl dithiophosphate ligands with somewhat longer zinc–sulphur distances than those within the $Zn_4S$ unit [ligand 1, Zn(1)–S(4) 2.341(4), Zn(2)–S(3) 2.353(4); ligand 2, Zn(2)–S(1) 2.335(3), Zn(2)–S(2) = 2.337(3) Å], but very similar to those found in the polymeric structure of 'zinc bis(*O*,*O'*-diethyl phosphorodithioate)'[19] where the bridging metal–sulphur bond lengths are 2.345(4) and 2.337(7)°, respectively. The resultant co-ordination at zinc is very close to ideal tetrahedral [angles at Zn(1)] 108.8(1) and 110.2(1), mean 109.5°; angles at Zn(2) 106.9(2)—111.8(1), mean 109.65°].

The structural features of the two independent dithiophosphate ligands are very similar to each other and to those found in other bis(*O*,*O'*-dialkyl dithiophosphato)zinc(II) compounds. However, the angles subtended at the phosphorus by the sulphur atoms are significantly opened [S–P–S 120.5(2), 121.1(2)°] compared to the bridging dithiophosphate ligands in the 'zinc bis(*O*,*O'*-diethyl phosphorodithioate)'[19] [108.0(3)°] and its isopropyl analogue[20] [117.3(3)°].

These variations reflect the relatively high degree of flexibility in the dithiophosphate ligand conferring an ability for the ligand to bond equally well in a variety of situations. Other dimensions in the two ligands are normal.

The structures of few zinc-containing cluster compounds have been described. That of 'basic' zinc acetate, $Zn_4(O_2CMe)_6O$,[21] contains the analogous $Zn_4O$ central tetrahedral core, whilst a very brief report[22] of the compound $Zn_4(S_2AsMe_2)_6S$ indicates that it too has a structure very similar to that of $Zn_4[S_2P(OEt)_2]_6S$, although no numerical data were included. Several compounds incorporate bridging thiolate groups, including pentameric methyl(t-butylthio)zinc(II),[23] octameric (isopropylthio)methylzinc(II),[24] *catena*-(μ-SPh)$[Zn_4(\mu\text{-}SPh)_6(MeOH)(SPh)]$,[25] and the anion $[Zn_{10}S_4(SPh)_{16}]^{4-}$.[26]

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