DALTON
FULL PAPER

Structural characterisation of basic zinc *O*,*O*′-dialkyl dithiophosphate and two isomeric examples of zinc monothiophosphates

Stefan Menzer,[a] Julian R. Phillips,[a] Alexandra M. Z. Slawin,[b] David J. Williams[a] and J. Derek Woollins*[b]

[a] *Department of Chemistry, Imperial College, South Kensington, London, UK SW7 2AY*
[b] *Department of Chemistry, University of St Andrews, St Andrews, Fife, UK KY16 9ST. E-mail: j.d.woollins@st-andrews.ac.uk*

Received 16th May 2000, Accepted 10th July 2000
First published as an Advance Article on the web 11th September 2000

The crystal structure of basic $Zn_4O[S_2P(OBu^i)_2]_6$ revealed a Zn_4O core. Two examples of zinc monothiophosphates, $Zn_4[O(S)P(OPh)_2]_6O$ and $Zn_4[O(S)P(OMe)_2]_6O$, have also been synthesized and structurally characterised. These systems also contain a Zn_4O core but display an interesting isomerism as a consequence of the unsymmetrical *O*,*S* donor ligands.

The structure of 'basic' zinc *O*,*O*′-dialkyl dithiophosphates (ZDDPs *i.e.* Zinc complexes of Dialkyl DithioPhosphates, $L = (RO)_2PS_2]^-$) has remained a matter of speculation for more than 30 years despite the commercial importance of these compounds as oil additives. In 1965 a tentative structure derived from unit cell volume/density was postulated[1] for the ^{i}Pr derivative; this and further EXAFS investigations[2] suggested that the structure was based on a tetrahedron of zinc atoms analogous to the pattern observed in basic zinc acetate[3] and beryllium acetate structures.[4] Here, we describe the structure of examples of both 'neutral' $Zn[S_2P(OBu^i)_2]_2$ **1** and basic ZDDPs $Zn_4O[S_2P(OBu^i)_2]_6$ **2** together with the synthesis and structures of two zinc monothiophosphate (ZDMP) derivatives $Zn_4O[O(S)P(OPh)_2]_6$ **3** and $Zn_4O[O(S)P(OMe)_2]_6$ **4** which also display the Zn_4O core but with the potential for interesting isomerism as a consequence of the unsymmetrical ligands.

Experimental

Complexes **1** and **2** were obtained from Exxon Chemicals.

Basic zinc *O*,*O*′-diphenyl monothiophosphate, $Zn_4O[OSP(OPh)_2]_6$

Sodium *O*,*O*-diphenyl monothiophosphate (2.5 g) was treated with dilute HCl (3 M, 200 cm^3) and the resulting solution extracted into diethyl ether (100 cm^3). The solvent was removed and the resulting oil dissolved in thf (50 cm^3); solid ZnO (0.5 g) was added and heated to reflux for 3 h. The resulting solution was cooled, filtered and the solvent removed *in vacuo*. The product was recrystallised from CH_2Cl_2–hexane. $Zn_4O[O(S)P(OPh)_2]_6$: yield 2.0 g, 74%. Found: C, 46.01; H, 3.01. $C_{72}H_{60}O_{19}P_6S_6Zn_4$ requires C, 46.27; H, 3.24%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 41.04 (s). $\tilde{\nu}_{max}/cm^{-1}$ 656 and 630 (PS), 1189 (PO) and 940 (P–O–C).

Basic zinc *O*,*O*-dimethyl monothiophosphate, $Zn_4O[OSP(OMe)_2]_6$ was prepared in a similar fashion to the above. Yield 1.28 g, 66%. Found: C, 12.99, H, 2.98. $C_{12}H_{36}O_{19}P_6S_6Zn_4$ requires C, 12.82, H, 3.23%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 50.5 (s). $\tilde{\nu}_{max}/cm^{-1}$ 616 (PS), 1150 and 1131 (PO), 1069 and 1034 (P–O–C).

Crystallography

Samples of the basic and neutral ZDDP were obtained by repeated fractional recrystallisation from hexane. Details of the X-ray data collections and refinements are given in Table 1. The data for compound **1** were collected at −70 °C, lower temperatures resulting in the crystals shattering. All data collections used Cu-Kα radiation, for **1** and **2** on a Siemens P4(RA) diffractometer and in the case of **3** and **4** on Siemens P4 and Rigaku AFC7S diffractometers respectively. Compounds **1**, **2** and **4** were corrected for absorption by semiempirical methods (psi scans) whilst for **3** a numerical (face-index) correction was applied. There is considerable disorder in the peripheral Bu^i groups in **1** and **2** which has been resolved into alternate partial occupancy orientations; the major occupancy atoms were refined anisotropically whilst the minor occupancy atoms were refined isotropically. In **3** there is no disorder and all of the atoms of the complex were refined anisotropically; the partial occupancy water of crystallisation was refined isotropically. In **4** the molecule is disposed about a $\bar{3}$ axis and consequently the zinc atoms occupy alternative sites so as to create two half weight interpenetrating tetrahedra. There is considerable thermal motion/disorder in the structure of **4** which is most apparent in the OMe groups. Attempts to model this disorder were unsuccessful; attempts to determine the structure of **4** at low temperature failed because of crystal fracturing. In all four structures the hydrogen atoms were placed in calculated positions. The structures were refined conventionally using SHELXTL[5] (**1**, **2** and **3**) and TEXSAN[6] (**4**).

CCDC reference number 186/2084.

Results and discussion

ZDDP Complexes

The X-ray analysis of neutral Bu^i ZDDP **1** shows it to have one of the typical core structures reported previously[7] for the ZnL_2 (L = DDP) system. The molecule has an overall binuclear structure (Fig. 1, Table 2) comprising a central eight-membered $Zn_2S_4P_2$ core (two bridging DDP ligands) spiro to two four-membered ZnS_2P ring systems. The complex has molecular C_2 symmetry about an axis passing through the centre of the eight membered ring and perpendicular to the four sulfur atoms. The eight membered ring has a twisted boat conformation, the Zn(1)–S(4)–P(2)–S(3) and Zn(2)–S(2)–P(1)–S(1) planes being inclined by *ca.* 50° to each other (the atoms comprising each plane are coplanar to within 0.1 Å). The non-bonded Zn(1) ···

Table 1

	1	2	3	4
Empirical formula	$C_{32}H_{72}O_8P_4S_8Zn_2$	$C_{48}H_{108}O_{13}P_6S_{12}Zn_4$	$C_{72}H_{61}O_{19.5}P_6S_6Zn_4$	$C_{12}H_{36}O_{19}P_6S_6Zn_4$
Formula weight	1096.0	1725.4	1877.9	1124.1
Crystal system	Triclinic	Orthorhombic	Rhombohedral	Rhombohedral
Space group	$P\bar{1}$	$P2_12_12_1$	$R\bar{3}$	$R\bar{3}$
T/°C	−70	−100	20	20
a/Å	10.3652(7)	13.447(2)	22.213(7)	17.956(8)
b/Å	11.3668(7)	22.734(6)		
c/Å	25.599(2)	26.839(6)	28.021(14)	10.79(1)
α/°	86.473(5)			
β/°	86.662(4)			
γ/°	65.324(7)			
V/Å^3	2734(1)	8205(3)	11977(9)	3011(2)
Z	2	4	6	3
μ/mm^{-1}	5.4	5.7	4.5	8.5
Measured/independent reflections/R_{int}	8666/8141/0.028	7416/7416/0	4058/3724/0.0494	1126/1010/0.0875
Final R (R_w)	6.94 (19.02)[a]	6.19 (16.1)[a]	4.68 (5.14)[b]	11.37 (27.56)[b]

[a] Refined against F. [b] Refined against F^2.

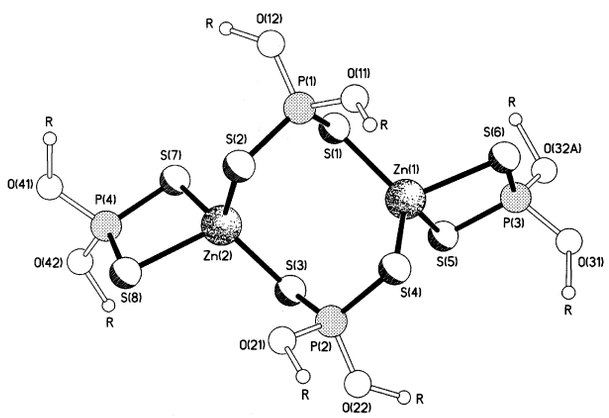

Fig. 1 The crystal structure of neutral $Zn_2[S_2P(O\ Bu^i)_2]_4$ **1**; only the first carbon atom of each Bu^i is illustrated (denoted R) for clarity.

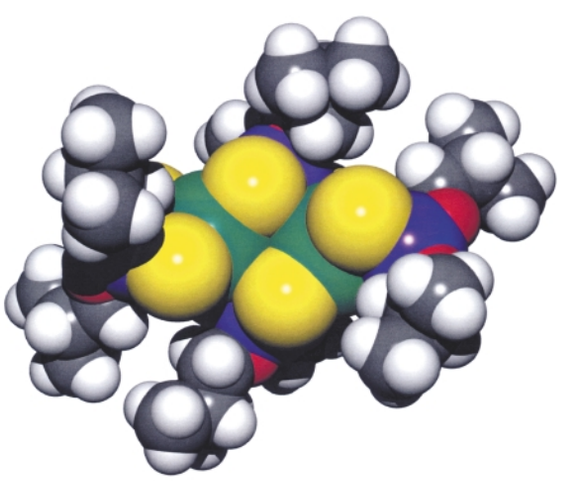

Fig. 2 Space filling representation of the structure of $Zn_2[S_2P(OBu^i)_2]_4$ **1** showing the prominence of four sulfur atoms on one face of the molecule.

Zn(2) distance in **1** is 4.16 Å [*cf.* the Pr^i analogue[8] where the Zn · · · Zn distance is 4.11 Å]. The geometry at each zinc centre is appreciably distorted from tetrahedral with angles ranging between 86.1 and 121.8° [Zn(1)] and 85.6 and 122.6° [Zn(2)], the acute angle in each case being associated with the small bite of the chelate ligand in the ZnS_2P rings. Within these four-membered rings the transannular S · · · S distances are 3.26 and 3.23 Å for Zn(1) and Zn(2) respectively.

Table 2 Selected bond lengths (Å) and angles (°) for neutral $Zn_2[S_2P(OBu^i)_2]_4$ **1**

Zn(1)–S(1)	2.317(2)	Zn(1)–S(4)	2.313(2)
Zn(1)–S(5)	2.355(2)	Zn(1)–S(6)	2.414(2)
Zn(2)–S(3)	2.317(2)	Zn(2)–S(2)	2.311(2)
Zn(2)–S(8)	2.403(2)	Zn(2)–S(7)	2.357(2)
P(1)–S(1)	1.978(3)	P(1)–S(2)	1.973(3)
P(2)–S(3)	1.977(3)	P(2)–S(4)	1.975(3)
P(3)–S(5)	1.988(3)	P(3)–S(6)	1.973(4)
P(4)–S(7)	1.983(3)	P(4)–S(8)	1.965(4)
S(4)–Zn(1)–S(1)	121.8(1)	S(4)–Zn(1)–S(5)	115.5(1)
S(1)–Zn(1)–S(5)	110.7(1)	S(4)–Zn(1)–S(6)	104.1(9)
S(1)–Zn(1)–S(6)	112.6(1)	S(5)–Zn(1)–S(6)	86.1(1)
S(2)–Zn(2)–S(3)	122.6(1)	S(2)–Zn(2)–S(7)	116.7(1)
S(3)–Zn(2)–S(7)	108.7(1)	S(2)–Zn(2)–S(8)	105.1(1)
S(3)–Zn(2)–S(8)	111.8(1)	S(7)–Zn(2)–S(8)	85.6(1)
P(1)–S(1)–Zn(1)	102.9(1)	P(1)–S(2)–Zn(2)	102.1(1)
P(2)–S(3)–Zn(2)	101.8(1)	P(2)–S(4)–Zn(1)	101.3(1)
P(3)–S(5)–Zn(1)	82.3(1)	P(3)–S(6)–Zn(1)	81.0(1)
P(4)–S(7)–Zn(2)	82.7(1)	P(4)–S(8)–Zn(2)	81.8(1)
S(1)–P(1)–S(2)	116.9(1)	S(3)–P(2)–S(4)	117.0(1)
S(5)–P(3)–S(6)	110.6(1)	S(7)–P(4)–S(8)	109.9(1)

A consequence of the twisted boat conformation in the central eight membered ring is the presence of two quite distinct faces to the molecule. One contains four prominent rhombically arranged sulfur atoms (Fig. 2) whereas those on the other face are shielded by the Bu^i groups, an effect that would presumably increase markedly with bulkier R groups. One can envisage that the 'sulfur face' is well organised for surface co-ordination onto appropriate metal arrays during the application of the ZDDP as an oil additive. The rhombic array of S(1), S(3), S(5) and S(7) has sides of 3.80–4.01 Å and an acute angle of *ca.* 60° which although not an optimal fit for surface co-ordination to iron (Fe–Fe distance *ca.* 2.5 Å in a body centred cubic (b.c.c.) or face centred cubic (f.c.c.) lattice depending on form/temperature) would still allow good contact. In this context one can conjecture that the highly congested Bu^t complex would be less able to surface co-ordinate and consequently would be a less useful oil additive.

Many differently substituted thiophosphates have been synthesized [R = alkyl or aryl] and there has been considerable speculation about the structure of the so called 'basic' ZDDPs . We have obtained good quality data from a single crystal at −100 °C and it reveals that for **2** (R = Bu^i the molecule does indeed contain a central Zn_4O core. The structure is chiral, indicating spontaneous resolution upon crystallisation has occurred. The core comprises (Fig. 3, Table 3) four zinc atoms in an almost perfect tetrahedral arrangement (the Zn · · · Zn

Table 3 Selected bond lenghts (Å) and angles (°) for basic $Zn_4O[S_2P(OBu^i)_2]_6$

Zn(1)–O	1.964(6)	Zn(2)–O	1.966(3)
Zn(3)–O	1.974(6)	Zn(4)–O	1.963(6)
Zn(1)–S(1)	2.337(3)	Zn(1)–S(6)	2.341(3)
Zn(1)–S(7)	2.343(3)	Zn(2)–S(2)	2.346(3)
Zn(2)–S(3)	2.348(3)	Zn(2)–S(9)	2.334(3)
Zn(3)–S(4)	2.335(3)	Zn(3)–S(5)	2.362(3)
Zn(3)–S(11)	2.347(3)	Zn(4)–S(8)	2.345(3)
Zn(4)–S(10)	2.368(3)	Zn(4)–S(12)	2.352(3)
P(1)–S(1)	1.975(4)	P(1)–S(2)	1.967(4)
P(2)–S(3)	1.981(4)	P(2)–S(4)	1.991(4)
P(3)–S(5)	1.962(4)	P(2)–S(6)	1.994(4)
P(3)–S(7)	1.978(4)	P(4)–S(8)	1.977(4)
P(5)–S(9)	1.983(4)	P(5)–S(10)	1.980(4)
P(6)–S(11)	1.980(5)	P(6)–S(12)	1.970(5)
Zn(1)–O–Zn(2)	110.1(3)	Zn(3)–O–Zn(4)	108.8(3)
Zn(1)–O–Zn(4)	109.6(3)	Zn(2)–O–Zn(4)	109.9(3)
Zn(1)–O–Zn(3)	108.9(3)	Zn(2)–O–Zn(3)	109.(3)
S(1)–P(1)–S(2)	118.8(2)	S(3)–P(2)–S(4)	117.9(2)
S(5)–P(3)–S(6)	117.6(2)	S(7)–P(4)–S(8)	117.3(2)
S(9)–P(5)–S(10)	117.2(9)	S(11)–P(6)–S(12)	117.6(2)
O–Zn(1)–S(1)	114.1(2)	O–Zn(1)–S(6)	112.6(2)
S(1)–Zn(1)–S(6)	107.7(1)	O–Zn(1)–S(7)	108.5(1)
S(1)–Zn(1)–S(7)	105.2(1)	S(6)–Zn(1)–S(7)	108.4(1)
O–Zn(2)–S(9)	112.6(2)	O–Zn(2)–S(2)	109.1(2)
S(2)–Zn(2)–S(3)	105.7(1)	O–Zn(2)–S(3)	111.3(2)
S(2)–Zn(2)–S(9)	107.3(1)	S(3)–Zn(2)–S(9)	110.5(1)
O–Zn(3)–S(4)	115.2(2)	O–Zn(3)–S(11)	110.5(2)
S(4)–Zn(3)–S(11)	107.0(1)	O–Zn(3)–S(5)	110.1(2)
S(4)–Zn(3)–S(5)	104.4(1)	S(11)–Zn(3)–S(5)	109.5(1)
O–Zn(4)–S(8)	116.8(2)	O–Zn(4)–S(12)	109.9(2)
S(8)–Zn(4)–S(12)	105.1(1)	O–Zn(4)–S(10)	109.0(2)
S(8)–Zn(4)–S(10)	108.0(1)	S(1)–Zn(4)–S(12)	107.8(1)

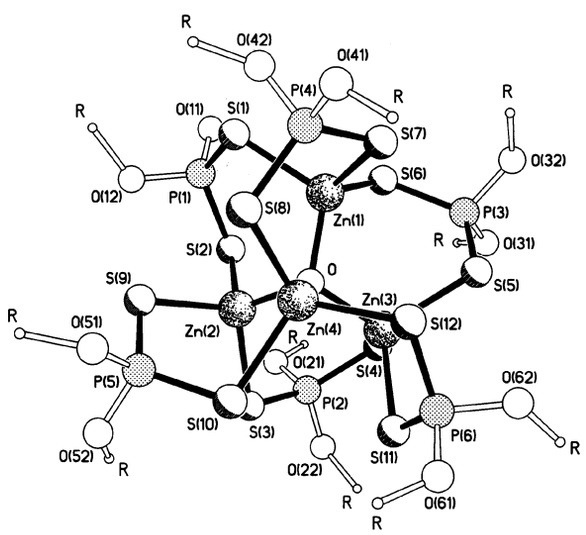

Fig. 3 The crystal structure of basic $Zn_4O[S_2P(OBu^i)_2]_6$ **2**; only the first carbon atom of each Bu^i is illustrated (denoted R) for clarity.

distances average 3.21 Å with inter-zinc angles of 60 ± 0.3°) about a central oxygen; the six edges of the Zn_4 tetrahedron are bridged by DDP groups with the ligands having a distinct and common helicity. The geometry at each zinc centre is only slightly distorted from tetrahedral with angles ranging between 104.3 and 116.8°; also the S–Zn–S angles are all very close to tetrahedral. The Zn–O distances lie in the range 1.963(6)–1.974(6) Å which appears to be slightly shorter than the Zn–O distances for binary zinc oxides [range 1.97–1.99 Å for tetrahedral zinc centres].[9] The Zn_4 core appears to be very close to the perfect size to accommodate edge bridging $[(RO)_2PS_2]^-$ ligands. However, attempts by us to prepare analogous tetranuclear complexes by making use of the related (but larger bite size) $(R_2PS)_2NH$ ligands have so far proved unsuccessful.

There has been a report[10] of the structure of a related $Zn_4S[S_2P(OEt)_2]_6$ system which has a similar overall geometry to the basic ZDDP with the core oxygen having been replaced by a sulfur atom. The Zn · · · Zn separation in this Zn_4S system is increased to 3.70 Å but, surprisingly, there is no evidence of flattening of the S_3Zn basal co-ordination. Interestingly the Zn–S distances to the core sulfur are 2.264(6) and 2.267(2) Å, both slightly shorter than those for binary zinc sulfides [range 2.31–2.36 Å]. Thus it appears that the tetrahedra in both the Zn_4O and Zn_4S cases are contracted from the 'natural' distances in the related binary compounds.

ZDMP Complexes

Zinc *O*,*O*′-dialkyl monothiophosphates (ZDMPs) can be obtained by direct reaction of a dialkyl phosphite with sulfur and zinc oxide.[11] However, we have found that this route is ineffective for dimethyl or diphenyl phosphite. Neutralisation of *O*,*O*′-dimethyl or *O*,*O*′-diphenyl thiophosphate with zinc oxide does give the basic complex $Zn_4O[O(S)P(OR)_2]_6$, analogous to those seen for the *O*,*O*′-dialkyl dithiophosphates[12] according to eqn. (1). These 'basic' Zn_4OL_6 complexes differ

$$6\ (RO)_2P(S)OH + 4\ ZnO \longrightarrow Zn_4O[O(S)P(OR)_2]_6 + 3\ H_2O \quad (1)$$

R = Ph **3**, R = Me **4**

from all of the similar complexes which have been reported previously in that there is no evidence of the corresponding 'neutral' ZnL_2 counterparts. With the dithiophosphates the ^{31}P NMR spectra of the basic complexes invariably include a peak due to the neutral complex (even very pure samples eliminate zinc oxide on dissolution to give traces of the neutral complex[13]). In contrast, the basic complexes **3** and **4** are the sole products of the above reaction, their ^{31}P NMR spectra contain only one peak at δ 41.0 and 50.5 for the phenyl and methyl derivatives respectively. Even if an excess of monothiophosphoric acid is used the basic complex is still the only reaction product.

$Zn_4O[O(S)P(OPh)_2]_6$ **3** and $Zn_4O[O(S)P(OMe)_2]_6$ **4** are both colourless solids which crystallise as rhombic needles. X-Ray analysis reveals that the core structure of **3** is remarkably similar to that of basic ZDDP **2**. The structure has crystallographic C_3 symmetry and the same central tetrahedral Zn_4O core as in **2** with the radiating bidentate ligands linking helically from the 'apical' Zn(2) atom to the three basal zinc atoms. Whereas the co-ordination of the apical zinc is $ZnOS_3$, all of the basal zinc atoms have a ZnO_3S pattern of co-ordination (Fig. 4). In **3** there are equal numbers of *R* and *S* isomers, no spontaneous resolution having occurred upon crystallisation. The Zn–S distances [range 2.310(2)–2.361(2) Å] (Table 4) are comparable to those in **2** [range 2.334(3)–2.368(3) Å]. Perhaps the most noticeable differences within the structure of **3** are in the distances from the zinc atoms to the central oxygen. The distance to the apical ($ZnOS_3$) atom is 2.010(5) Å whereas those to the basal (ZnO_3S) atoms are 1.971(2) Å which are more in accord with the distances in **2**. The central oxygen atom in **3** has almost perfect tetrahedral angles with the distortions in the Zn–O bond lengths being accommodated by an axial distortion of the tetrahedron. The Zn · · · Zn distances along the vertical sides of the tetrahedron are *ca.* 3.250 Å whilst those around the base are 3.218 Å, with the basal distance being the same as the Zn · · · Zn separations in **2**. Whereas the angles at the apical zinc [Zn(2)] are almost perfectly tetrahedral [range 109.1(1)–109.8(1)°] those at the basal zinc atoms are substantially distorted [range 104.1(1)–120.2(1)°], though the reason for this asymmetry is not immediately apparent. We speculate that it may be a function of the flexibility of the six-membered Zn_2OPOS rings coupled with the packing constraints of the OPh groups. The

Table 4 Selected bond lengths (Å) and angles for $Zn_4O[O(S)P(OPh)_2]_6$

Zn(1)–S(2)	2.310(2)	P(3)–O(5)	1.577(5)
Zn(1)–O(10)	1.971(2)	P(3)–O(4)	1.572(5)
Zn(1)–O(6)	1.968(4)	P(3)–O(7)	1.484(3)
Zn(1)–O(7b)	1.961(3)	P(1)–S(1)	1.984(3)
Zn(2)–S(1)	2.361(2)	P(1)–O(3)	1.587(3)
Zn(2)–O(10)	2.010(5)	P(1)–O(2)	1.575(5)
P(3)–S(2)	1.976(2)	P(1)–O(6b)	1.477(4)
S(2)–Zn(1)–O(10)	120.2(1)	O(4)–P(3)–O(7)	104.6(2)
S(2)–Zn(1)–O(6)	104.1(1)	Zn(1)–S(2)–P(3)	96.4(1)
O(10)–Zn(1)–O(6)	111.9(2)	S(1)–P(1)–O(3)	109.9(2)
S(2)–Zn(1)–O(7b)	106.3(1)	S(1)–P(1)–O(2)	113.4(2)
O(10)–Zn(1)–O(7b)	107.1(2)	O(3)–P(1)–O(2)	100.2(2)
O(6)–Zn(1)–O(7b)	106.4(2)	S(1)–P(1)–O(6b)	116.7(1)
S(1)–Zn(2)–O(10)	109.2(1)	O(3)–P(1)–O(6b)	110.0(2)
S(1)–Zn(2)–S(1a)	109.8(1)	O(2)–P(1)–O(6b)	105.3(2)
O(10)–Zn(2)–S(1a)	109.1(1)	Zn(2)–S(1)–P(1)	100.4(1)
S(2)–P(3)–O(5)	102.2(2)	Zn(1)–O(10)–Zn(2)	109.5(1)
S(2)–P(3)–O(4)	114.5(2)	Zn(1)–O(10)–Zn(1a)	109.5(1)
O(5)–P(3)–O(4)	105.7(2)	Zn(1)–O(6)–P(1a)	139.3(2)
S(2)–P(3)–O(7)	116.3(2)	P(3)–O(7)–Zn(1a)	138.7(2)
O(5)–P(3)–O(7)	113.4(3)		

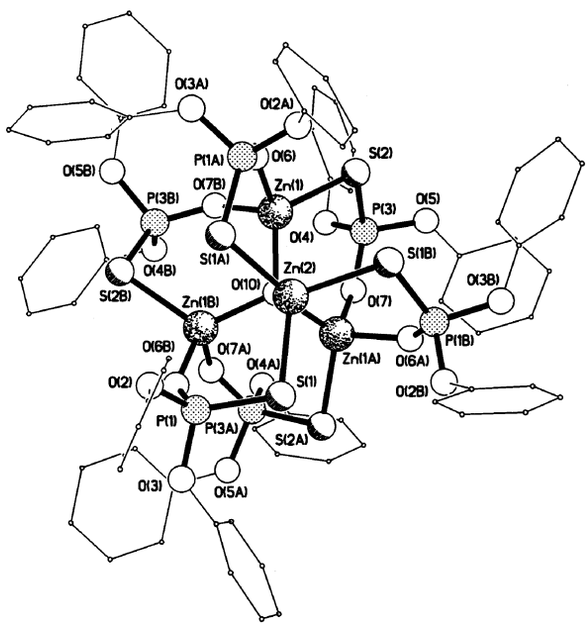

Fig. 4 The crystal structure of $Zn_4O[O(S)P(OPh)_2]_6$ **3**.

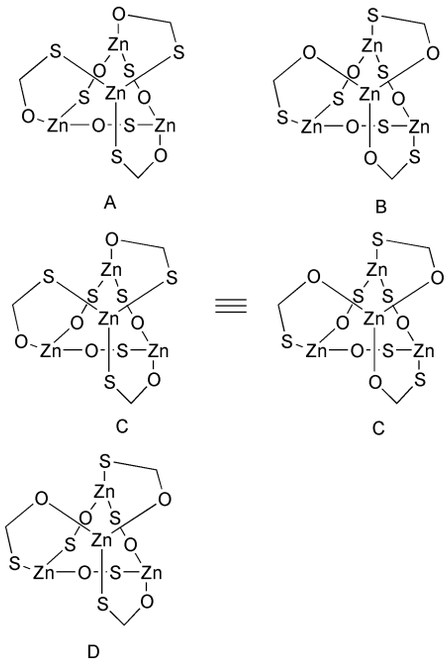

Fig. 5 Schematic illustrating possible isomers for $Zn_4O[O(S)P(OR)_2]_6$.

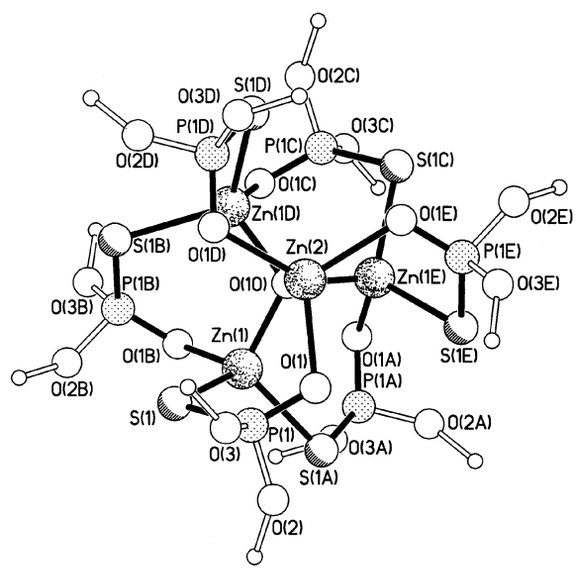

Fig. 6 The crystal structure of $Zn_4O[O(S)P(OMe)_2]_6$ **4**.

intermolecular packing is dominated by weak aromatic–aromatic edge–face and face–face interactions.

An important difference between the monothiophosphates and the dithiophosphates is that, because of the ambidentate nature of the ligand, the zinc atoms cannot all be equivalent. The possible structural arrangements are as follows. [i] A complex (Fig. 5 type **A**) with one apical zinc atom co-ordinated to the central oxygen and by three sulfur atoms from the thiophosphate ligands. The three basal zinc atoms are then each co-ordinated to the central oxygen and to two oxygen atoms and a sulfur from thiophosphate ligands. The reverse of this arrangement is also possible, with the apical zinc atom co-ordinated to four oxygen atoms (type **B**). [ii] A complex in which the apical zinc has a $ZnOS_3$ co-ordination with the basal zinc atoms having different co-ordination spheres (type **C**). [iii] A complex with two pairs of distinct zinc atoms in which one pair have a co-ordination sphere made up of two sulfur and two oxygen atoms and the other pair are co-ordinated to three oxygen atoms and one sulfur (type **D**). There are thus (ignoring enantiomers) four potential isomers provided one assumes that the Zn–O–P–S–P–Zn rings are planar. Whereas **A** and **B** possess a threefold rotational axis along the apical zinc–central oxygen bond, **C** and **D** have only C_1 symmetry. In practice the Zn–O–P–S–P–Zn rings are non-planar and thus each chelate ring can have either a δ or λ configuration and hence there can be Δ and Λ forms possible for each of the tetranuclear structures shown in Fig. 5.

Using the above classification compound **3** has a type **A** configuration. Interestingly the crystal structure of **4** reveals it to have a type **B** structure (Fig. 6, Table 5). The quality of the the data precludes a detailed discussion of the structure but it does demonstrate the ability of this system to produce different isomers. Perhaps the most surprising feature is that in both **3** and **4** we have been able to crystallise a single isomer (and its enantiomer). In the two examples of basic zinc monothiophosphinate complexes which have been studied previously ($Zn_4O(OSPEt_2)_6$ and $Zn_4O(OSPBu^n_2)_6$), the space group of both complexes was assigned as *R*3 suggesting them to be of type **A** or **B**, however the structures were not solved and it is not

Table 5 Selected bond lengths (Å) and angles (°) for $Zn_4O[O(S)P(OMe)_2]_6$

Zn(1)–O(10)	1.944(3)	Zn(1)–S(1)	2.370(4)
Zn(1)–O(1)	2.343(10)	Zn(2)–O(10)	2.035(4)
Zn(2)–O(1)	2.196(10)	P(1)–S(1)	1.952(5)
P(1)–O(2)	1.492(14)	P(1)–O(3)	1.521(12)
Zn(1)–O(10)–Zn(2)	106.5(1)	Zn(1)–O(10)–Zn(1′)	112.3(1)
O(1)–Zn(2)–O(1′)	113.4(3)	O(1)–Zn(2)–O(10)	105.2(3)
S(1)–Zn(1)–O(1)	110.5(2)	S(1)–Zn(1)–S(1′)	114.4(1)
O(1)–P(1)–S(1)	122.1(4)	Zn(2)–O(1)–P(1)	114.6(5)
P(1)–S(1)–Zn(1)	96.2(2)		

known whether the apical zinc is surrounded by oxygen or sulfur atoms.[14]

Acknowledgements

We are grateful to EXXON Chemicals for support, to the Joint Research Equipment Initiative for an equipment grant and wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

References

1 A. J. Burn and G. W. Smith, *Chem. Commun.*, 1965, 394.
2 A. J. Burn, R. W. Joiner, P. Meechan and K. M. A. Parker, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 982.
3 H. Koyama and V. Saito, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 112.
4 A. Tulinsky, C. R. Worthington and E. Pignataro, *Acta Crystallogr.*, 1959, **12**, 623.
5 SHELXTL 5.1, Bruker AXS, Madison, WI, 1999.
6 TEXSAN, Molecular Structure Corporation, The Woodlands, TX, 1994, 1997.
7 I. Haiduc and D. B. Sowerby, *Polyhedron*, 1995, **14**, 3389; I. Haiduc and D. B. Sowerby, *Polyhedron*, 1996, **15**, 2469.
8 S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 1969, **8**, 2410.
9 The United Kingdom Chemical Database Service, D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746.
10 P. G. Harrison, M. J. Begley, T. Kikabhai and F. Killer, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 925.
11 J. R. Phillips, J. C. Poat, A. M. Z. Slawin, D. J. Williams, P. T. Wood and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2369.
12 A. J. Burn, S. K. Dewan, I. Gosney and P. S. G. Tan, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 753.
13 A. J. Burn, S. K. Dewan, I. Gosney and P. S. G. Tan, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 1311.
14 S. Meriani, G. Nardin and A. Ripamonti, *Inorg. Chem.*, 1967, **6**, 1931.