Zinc(II) Bis(*O,O*′-dialkyl dithiophosphates): Complexation Behaviour with Pyridine and Other Multidentate Nitrogen Donor Molecules. The Crystal and Molecular Structures of the 1:1 Complexes of Bis(*O,O*′-di-isopropyl dithiophosphato)zinc(II) with Pyridine, 2,2′-Bipyridine, and 2,2′:6′,2″-Terpyridine and of (1,11-Diamino-3,6,9-triazaundecane)zinc(II) Bis(*O,O*′-diethyl dithiophosphate)†

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Fifteen complexes of zinc(II) bis(*O,O*′-dialkyl dithiophosphates), $Zn[S_2P(OR)_2]_2$ (R = Et or Pr^i), with a variety of nitrogen donor ligands, L [L = pyridine (py), pyridazine (pydz), ethylenediamine (en), 2,2′-bipyridine (bipy), *N,N*′-diethylethylenediamine (deen), 1,10-phenanthroline (phen), 2,2′:6′,2″-terpyridine (terpy), and 1,11-diamino-3,6,9-triazaundecane (datau)], all of 1:1 stoicheiometry, have been synthesised. The crystal structures of four, $Zn[S_2P(OPr^i)_2]_2 \cdot L$ [L = py (**1**), bipy (**2**), or terpy (**3**)] and the datau complex of $Zn[S_2P(OEt)_2]_2$, (**4**), have been determined by the heavy-atom method with intensity data collected by a four-circle diffractometer using Mo-K_α radiation (λ = 0.7107 Å). Crystals of $Zn[S_2P(OPr^i)_2]_2 \cdot py$ are monoclinic, space group $P2_1/n$, with a = 16.289(3), b = 8.331(2), c = 21.316(3) Å, β = 99.56(2)°, Z = 4, final R = 0.0499 from 3 558 independent reflections. Crystals of $Zn[S_2P(OPr^i)_2]_2 \cdot bipy$ are triclinic, space group $P\bar{1}$, with a = 9.020(2), b = 8.502(2), c = 21.267(2) Å, α = 83.12(2), β = 97.96(2), γ = 103.46(2)°, Z = 2, final R = 0.0988 from 2 463 independent reflections. Crystals of $Zn[S_2P(OPr^i)_2]_2 \cdot terpy$ are monoclinic, space group $P2_1/n$, with a = 8.847(2), b = 25.215(2), c = 15.740(2) Å, β = 90.74(2)°, Z = 4, final R = 0.0988 from 3 959 independent reflections. Crystals of $[Zn(datau)][S_2P(OEt)_2]_2$ are monoclinic, space group $P2_1/c$, with a = 8.183(2), b = 25.161(2), c = 14.981(2) Å, β = 99.72(2)°, Z = 4, final R = 0.0616 from 3 068 independent reflections. The complexes (**1**)—(**3**) exhibit molecular structures in which the nitrogen donor ligand co-ordinates to the zinc atom. In (**1**), one $S_2P(OPr^i)_2$ ligand chelates the zinc almost symmetrically [Zn–S 2.352(2), 2.496(2) Å], whilst the other is strongly anisobidentate [Zn–S 2.273(2), 3.041(2) Å]. The pyridine nitrogen atom completes a distorted tetrahedral geometry about zinc [Zn–N 2.028(4) Å]. The zinc atom in (**2**) is chelated by the ligand [Zn–N 2.09(1), 2.14(1) Å], with one anisobidentate [Zn–S 2.365(5), 2.711(4) Å] and one unidentate [Zn–S 2.327(4), 3.822(5) Å] $S_2P(OPr^i)_2$ attached to the metal. Both $S_2P(OPr^i)_2$ groups are unidentate in (**3**) [Zn–S 2.334(4), 3.523(5) Å (ligand 1); 2.339(3), 3.977(5) Å (ligand 2)], with all three nitrogen atoms within bonding distance of the metal [Zn–N 2.21(1), 2.12(1), 2.17(1) Å]. The geometries at zinc in both (**2**) and (**3**) are irregular. Complexation of bis(*O,O*′-diethyl dithiophosphato)zinc(II) by datau results in the ionisation of both $S_2P(OEt)_2$ groups, and crystals of the complex comprise $[Zn(datau)]^{2+}$ cations and $S_2P(OEt)_2^-$ anions [closest Zn ··· S contact 4.153(3) Å]. All five of the nitrogen atoms of the datau ligand are bonded to the zinc in the cation to give a distorted trigonal-bipyramidal geometry [Zn–N 2.047(6)—2.191(6) Å; N_{eq}–Zn–N_{eq} angles 117.4(3), 115.5(3), 126.8(3)°; N_{ax}–Zn–N_{ax} angle 161.3(3)°]. The bonding parameters of the $S_2P(OR)_2$ groups exhibit small variations with the change in bonding environment in complexes (**1**)—(**4**). Principal ligand i.r. vibration data are also reported for the complexes and related compounds, and are remarkably insensitive as a probe for the mode of bonding.

In the preceding paper,[1] we described the preparation of four complexes of zinc(II) bis(*O,O*′-dialkyl dithiophosphates) with small nitrogen donor molecules, such as di- and tri-ethylamine. In this paper, we report a more comprehensive study of complexes of these compounds with a wide variety of nitrogen donor ligands of different donor capacity, including the *X*-ray crystal structures of four selected examples.

Experimental

The zinc(II) bis(*O,O*′-dialkyl dithiophosphates) were prepared as in the preceding paper.[1]

Syntheses of the Complexes.—All the syntheses were essentially similar, and only a general procedure is given. Physical and microanalytical data are collected in Table 1.

The appropriate amine (either as a neat liquid or dissolved in the minimum amount of ethanol; 4 × 10^{-4} mol) was added to the zinc(II) bis(*O,O*′-dialkyl dithiophosphates) (4 × 10^{-4} mol) also dissolved in ethanol (4 cm^3). After allowing the mixture to stand overnight at room temperature, the colourless, crystalline

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† *Supplementary data available* (No. SUP 56461, 11 pp.): thermal parameters, packing diagrams. 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. Physical and microanalytical (%) data

		Found			Calculated		
Compound	M.p. (°)	C	H	N	C	H	N
$Zn[S_2P(OEt)_2]_2$	74—76	21.85	4.55	—	22.05	4.65	—
$Zn[S_2P(OEt)_2]_2 \cdot py$	80	30.45	5.00	2.80	30.30	4.90	2.70
$Zn[S_2P(OEt)_2]_2 \cdot pydz$	58—64	28.75	4.75	6.20	27.95	4.70	5.45
$Zn[S_2P(OEt)_2]_2 \cdot en$	*	24.45	6.15	6.10	24.20	5.70	5.65
$Zn[S_2P(OEt)_2]_2 \cdot bipy$	107—108	36.75	4.90	4.75	36.50	4.75	4.75
$Zn[S_2P(OEt)_2]_2 \cdot deen$	89—90	30.55	6.65	5.15	30.45	6.55	5.05
$Zn[S_2P(OEt)_2]_2 \cdot phen$	146	38.90	4.55	4.85	39.00	4.60	4.55
$Zn[S_2P(OEt)_2]_2 \cdot terpy$	190	41.20	4.80	6.20	41.30	4.65	6.30
$[Zn(datau)][S_2P(OEt)_2]_2$	126—128	30.95	7.15	11.75	30.75	6.75	11.20
$Zn[S_2P(OPr^i)_2]_2$	140—142	29.10	5.85	—	29.30	5.75	
$Zn[S_2P(OPr^i)_2]_2 \cdot py$	81	35.90	6.00	2.75	35.75	6.20	2.45
$Zn[S_2P(OPr^i)_2]_2 \cdot pydz$	78—79	33.80	5.70	4.80	33.60	5.65	4.90
$Zn[S_2P(OPr^i)_2]_2 \cdot en$	67—68	30.55	6.65	4.50	30.45	6.55	5.05
$Zn[S_2P(OPr^i)_2]_2 \cdot bipy$	160—161	40.75	5.45	4.25	40.75	5.90	4.30
$Zn[S_2P(OPr^i)_2]_2 \cdot deen$	99—100	35.75	7.45	4.60	35.55	7.30	4.60
$Zn[S_2P(OPr^i)_2]_2 \cdot phen$	178	42.90	5.60	4.15	42.90	5.40	4.15
$Zn[S_2P(OPr^i)_2]_2 \cdot terpy$	206—208	44.75	5.65	5.65	44.70	5.40	5.80

* Viscous liquid at room temperature.

Table 2. Crystal data

	$Zn[S_2P(OPr^i)_2]\cdot py$	$Zn[S_2P(OPr^i)_2]_2 \cdot bipy$	$Zn[S_2P(OPr^i)_2]_2 \cdot terpy$	$[Zn(datau)][S_2P(OEt)_2]_2$
Formula	$C_{17}H_{33}NO_4P_2S_4Zn$	$C_{22}H_{36}N_2O_4P_2S_4Zn$	$C_{27}H_{39}N_3O_4P_2S_4Zn$	$C_{16}H_{43}N_5O_4P_2S_4Zn$
M	571.03	648.11	725.20	625.10
Crystal class	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$[a]	$P\bar{1}$	$P2_1/n$[a]	$P2_1/c$
a/Å	16.289(3)	9.020(2)	8.847(2)	8.183(2)
b/Å	8.331(2)	8.502(2)	25.215(2)	25.161(2)
c/Å	21.316(3)	21.267(2)	15.740(2)	14.981(2)
α/°		83.12(2)		
β/°	99.56(2)	97.96(2)	90.74(2)	99.72(2)
γ/°		103.46(2)		
U/Å^3	2 852(2)	1 564(1)	3 511(1)	3 040(1)
Z	4	2	4	4
D_m/g cm^{-3}	1.34[b]	1.47[c]	1.45[b]	1.42[c]
D_c/g cm^{-3}	1.33	1.38	1.37	1.36
$F(000)$	1 192	676	1 512	1 320
No. independent reflections	3 558	2 463	3 959	3 068
Final R	0.0499	0.0988	0.0988	0.0616
Crystal size (mm)	0.55 × 0.2 × 0.1	0.5 × 0.1 × 0.1	1.2 × 0.2 × 0.05	0.5 × 0.15 × 0.1
μ(Mo-K_α)/cm^{-1}	12.98	11.95	10.74	12.29
λ(Mo-K_α)/Å	0.7107	0.7107	0.7107	0.7107
Weighting scheme				
$A[0]$	175.44	76.56	108.53	−11.53
$A[1]$	219.23	107.54	149.45	−44.59
$A[2]$	38.28	41.95	50.46	−51.68
$A[3]$	−12.95	3.389	7.355	−25.07

[a] Equivalent positions $x, y, z; -x, -y, -z; x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}; -x - \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$. [b] Measured by flotation using hexachlorobuta-1,3-diene and hexane. [c] Measured by flotation using 1,2-dibromoethane and hexane.

complexes were filtered off, recrystallised from hot ethanol, washed with pentane, and dried in air.

Structure Determinations.—Suitable crystals of the complexes $Zn[S_2P(OPr^i)_2]_2 \cdot L$ [L = pyridine (py), 2,2′-bipyridine (bipy), or 2,2′:6′,2″-terpyridine (terpy)] and $[Zn(datau)][S_2P(OEt)_2]_2$ (datau = 1,11-diamino-3,6,9-triazaundecane) were mounted on glass capillaries and used for both oscillation and Weissenberg photography and the subsequent intensity data collection using a Hilger and Watts Y290 four-circle diffractometer. Crystal data for all four complexes are listed in Table 2. Accurate cell dimensions were determined by a least-squares refinement of 23 reflections. Reflection intensities were measured in the range $0 < \theta < 25°$ using Mo-K_α radiation, reflections with $I < 3\sigma(I)$ being considered unobserved. Lorentz and polarisation corrections were applied, but none for absorption due to the low μ values. The atomic scattering factors used were those for neutral atoms, with real and imaginary dispersion corrections being made for zinc, phosphorus, and sulphur.[2] Structures were solved by the usual procedures of the heavy-atom method, with the approximate position of the zinc atom being determined from a three-dimensional Patterson synthesis. Subsequent three-dimensional Fourier or difference Fourier syntheses phased on the zinc position revealed the positions of all

Table 3. Final fractional atomic co-ordinates for $Zn[S_2P(OPr^i)_2]_2{\cdot}py$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Zn(1)	0.558 24(4)	0.314 15(8)	0.354 42(3)
S(1)	0.690 17(9)	0.225 8(2)	0.354 10(7)
S(2)	0.653 85(9)	0.419 6(2)	0.482 57(7)
S(3)	0.506 76(9)	0.578 1(2)	0.342 64(7)
S(4)	0.487 64(9)	0.277 3(2)	0.242 16(7)
P(1)	0.737 38(8)	0.348 6(2)	0.433 03(7)
P(2)	0.450 07(8)	0.496 4(2)	0.257 88(7)
N(1)	0.483 6(3)	0.182 1(5)	0.401 7(2)
O(1)	0.794 6(2)	0.489 3(5)	0.415 7(2)
O(2)	0.805 4(2)	0.231 7(5)	0.469 4(5)
O(3)	0.460 2(2)	0.620 0(5)	0.204 0(2)
O(4)	0.353 1(2)	0.489 9(5)	0.252 6(2)
C(1)	0.476 7(4)	0.021 8(7)	0.393 9(3)
C(2)	0.425 6(4)	−0.069 5(7)	0.425 6(3)
C(3)	0.381 0(4)	0.004 3(8)	0.466 4(3)
C(4)	0.388 0(4)	0.169 5(8)	0.474 6(3)
C(5)	0.439 6(4)	0.253 7(7)	0.441 3(3)
C(6)	0.761 5(5)	0.644(1)	0.390 5(4)
C(7)	0.804 3(7)	0.772(1)	0.436 8(6)
C(8)	0.777 2(8)	0.655(2)	0.321 5(5)
C(9)	0.846 7(4)	0.263(1)	0.535 3(3)
C(10)	0.855 2(8)	0.106(2)	0.567 5(5)
C(11)	0.929 5(8)	0.331(2)	0.533 0(6)
C(12)	0.543 2(6)	0.682(1)	0.195 6(4)
C(13)	0.566 5(9)	0.609(2)	0.140 3(8)
C(14)	0.539(1)	0.848(2)	0.190(1)
C(15)	0.302 9(4)	0.638 0(8)	0.255 8(3)
C(16)	0.257 7(5)	0.617(1)	0.312 6(4)
C(17)	0.244 6(5)	0.647(1)	0.193 2(4)

remaining non-hydrogen light atoms. Final stages of refinement were performed with all atoms varying anisotropically (with the exceptions listed below) until convergence was achieved. A weighting scheme of the form shown below was applied for all

$$w = 1/\{A[0]{\cdot}T[0]'(\chi) + A[1]{\cdot}T[1]'(\chi) + A[2]{\cdot}T[2]'(\chi) + A[3]{\cdot}T[3]'(\chi)\}$$

the refinements, where the terms $A[I]$ ($I = 0, 1, 2, 3$) are the coefficients of a Chebyshev series in $T[I]'(\chi)$ [$\chi = F_o/F_o(\text{max.})$]. Values of the coefficients $A(I)$ are listed in Table 2.

Some difficulty was encountered in the refinement of a few peripheral atoms in the complexes with bipy and terpy due to disorder. In particular, refinement of the isopropoxy group comprising O(3), C(17), C(18), and C(19) of the bipy complex, and that comprising O(4), C(25), C(26), C(27), and S(4) of the terpy complex require further description.

In the case of the bipy complex, a difference-Fourier synthesis after the application of the weighting scheme revealed one major peak (0.87 e Å^{-3}) which was very close to O(3) [1.22(3) Å] and C(17) [1.23(3) Å]. In addition, the thermal parameters of the isopropyl group carbon atoms C(17), C(18), and C(19) [0.16(2), 0.18(1), and 0.17(1) Å^2, respectively] were higher than those found for the other isopropyl group carbon atoms. Furthermore, the geometry around O(3) was far from satisfactory. Atoms C(17), C(18), C(19), and O(3) were then deleted and refinement of the rest of the molecule continued with all atoms varying anisotropically to an *R* value of 0.1313. Examination of a difference-Fourier synthesis at this stage showed that the peak originally recognised as O(3) was quite ill defined, and was reassigned as an oxygen atom with an isotropic thermal parameter of 0.08 Å^2 (*i.e.* a value comparable to the other three oxygen atoms already located). A structure factor calculation (no refinement) gave an *R* value of 0.1259, and a difference-Fourier synthesis exhibited its largest peak (2.47 e Å^{-3}) at a distance of 1.82 Å from P(2). This peak was interpreted as a disordered sulphur atom and was assigned as S(5) with an occupancy factor of 0.1. The next three largest peaks in the Fourier synthesis (1.93, 1.84, and 1.84 e Å^{-3}) were assigned as the three carbon atoms, C(17), C(18), and C(19) of the isopropyl group. The occupancy factors of these three carbon atoms and of O(3) were changed from unity to 0.9, and constraints were placed around P(2) in order to prevent O(3) and S(5) from merging into one peak. Additionally, the occupancy factors of O(3) and S(5) were weighted such that the total occupancy was 1.0, although still allowing them to refine. Thus, with all atoms except O(3), S(5), C(17), C(18), and C(19) vibrating anisotropically the final *R* value was 0.0988. It was not possible to refine these atoms anisotropically due to the close proximity of atoms O(3), S(5), and C(17). The final refined occupancy factors of O(3) and S(5) were 0.85(4) and 0.15(4) respectively.

In the refinement of the structure of the terpy complex, anomalies were observed at an earlier stage. All non-hydrogen light atoms apart from two of the isopropyl group carbon atoms [C(26) and C(27)] were located from the initial three-dimensional Fourier synthesis, although from isotropic refinement at this stage it was apparent that the isotropic thermal parameter of S(4) [0.113(2) Å^2] was significantly higher than for the remaining three sulphur atoms [S(1) 0.049(1), S(2) 0.061(2), S(3) 0.080(2) Å^2]. Similarly, that for O(4) [0.203(9)] was higher than those for O(1) [0.057(4)], O(2) [0.054(4)], and O(3) [0.131(7) Å^2]. Refinement with the carbon atoms varying isotropically and the remainder anisotropically, gave an *R* value of 0.1076; however, the geometry around O(4) was unsatisfactory. A difference-Fourier synthesis revealed one large peak (1.68 e Å^{-3}) 1.889(5) Å from P(2), which with atoms S(3), S(4), and O(3) completed approximate tetrahedral geometry about P(2). The carbon atoms C(25), C(26), and C(27) of the isopropyl group also exhibited high isotropic thermal parameters [0.23(2), 0.222(9), and 0.209(8) Å^2 respectively]. Further refinement (all atoms varying anisotropically) reduced the *R* value to 0.0957, and application of the weighting scheme produced an improvement to a value of 0.0948. However, the geometry at O(4) and its contiguous isopropyl group [C(25), C(26), and C(27)] was far from satisfactory, and therefore these atoms were deleted. Full-matrix anisotropic refinement of the rest of the structure excluding these atoms gave an *R* value of 0.1186, and a difference-Fourier synthesis showed that the peak originally assigned as O(4) was ill defined. The largest peak (2.832 e Å^{-3}) was assigned as O(4) with an isotropic thermal parameter of 0.08 Å^2 (*i.e.* comparable to the values of the other three oxygen atoms). A structure factor calculation at this stage gave an *R* value of 0.1205, and a difference-Fourier synthesis now yielded four outstanding peaks. Three of these were assigned as C(25), C(26), and C(27), whilst the fourth was assigned as a sulphur atom [S(5)] since it was 1.9 Å distant from P(2), around which is completed approximate tetrahedral co-ordination with S(3), S(4), and O(3). The occupancy factors of O(4), C(25), C(26), and C(27) were made equivalent, and that for S(5) weighted with respect to O(4) such that the sum for both was unity. The geometries around atoms P(2), O(4), and C(25) were constrained for further refinement. Thus, further

Table 4. Intramolecular bond distances (Å) and angles (°) for $Zn[S_2P(OPr^i)_2]_2$·py with estimated standard deviations in parentheses

Zn(1)–S(1)	2.273(2)	S(4)–P(2)	1.971(2)	O(4)–C(15)	1.488(7)	C(6)–C(8)	1.54(1)
Zn(1)–S(2)	3.041(2)	P(1)–O(1)	1.579(4)	N(1)–C(1)	1.348(7)	C(9)–C(10)	1.47(1)
Zn(1)–S(3)	2.352(2)	P(1)–O(2)	1.579(4)	N(1)–C(5)	1.334(7)	C(9)–C(11)	1.47(1)
Zn(1)–S(4)	2.496(2)	P(2)–O(3)	1.573(4)	C(1)–C(2)	1.384(8)	C(12)–C(13)	1.43(2)
Zn(1)–N(1)	2.028(4)	P(2)–O(4)	1.566(4)	C(2)–C(3)	1.368(9)	C(12)–C(14)	1.39(2)
S(1)–P(1)	2.010(2)	O(1)–C(6)	1.467(8)	C(3)–C(4)	1.390(9)	C(15)–C(16)	1.53(1)
S(2)–P(1)	1.948(2)	O(2)–C(9)	1.477(7)	C(4)–C(5)	1.379(8)	C(15)–C(17)	1.51(1)
S(3)–P(2)	2.007(2)	O(3)–C(12)	1.485(9)	C(6)–C(7)	1.54(1)		
S(1)–Zn(1)–S(2)	75.68(5)	Zn(1)–S(4)–P(2)	80.20(6)	P(1)–O(1)–C(6)	123.0(4)	O(1)–C(6)–C(7)	106.0(7)
S(1)–Zn(1)–S(3)	128.53(7)	S(1)–P(1)–S(2)	113.82(9)	P(1)–O(2)–C(9)	122.0(4)	O(1)–C(6)–C(8)	106.8(8)
S(1)–Zn(1)–S(4)	104.05(6)	S(3)–P(1)–S(4)	110.95(8)	P(2)–O(3)–C(12)	121.7(5)	C(7)–C(6)–C(8)	116.5(8)
S(1)–Zn(1)–N(1)	118.1(1)	S(1)–P(1)–O(1)	109.9(2)	P(2)–O(4)–C(15)	121.6(4)	O(2)–C(9)–C(10)	106.1(7)
S(2)–Zn(1)–S(3)	86.91(5)	S(2)–P(1)–O(1)	113.2(2)	Zn(1)–N(1)–C(1)	121.3(4)	O(2)–C(9)–C(11)	108.2(7)
S(2)–Zn(1)–S(4)	169.28(5)	O(1)–P(1)–O(2)	100.3(2)	Zn(1)–N(1)–C(5)	120.1(4)	C(10)–C(9)–C(11)	110.0(9)
S(2)–Zn(1)–N(1)	88.3(1)	S(1)–P(1)–O(2)	103.7(2)	C(1)–N(1)–C(5)	118.6(5)	O(3)–C(12)–C(13)	108.8(8)
S(3)–Zn(1)–S(4)	85.03(5)	S(2)–P(1)–O(2)	114.7(2)	N(1)–C(5)–C(4)	122.4(6)	O(3)–C(12)–C(14)	109(1)
S(3)–Zn(1)–N(1)	109.1(1)	S(3)–P(2)–O(3)	110.3(2)	C(5)–C(4)–C(3)	118.9(6)	C(13)–C(12)–C(14)	111(1)
S(4)–Zn(1)–N(4)	101.0(1)	S(4)–P(2)–O(3)	114.2(2)	C(4)–C(3)–C(2)	119.0(6)	O(4)–C(15)–C(16)	106.5(6)
Zn(1)–S(1)–P(1)	93.63(7)	O(3)–P(2)–O(4)	101.4(2)	C(3)–C(2)–C(1)	119.3(6)	O(4)–C(15)–C(17)	105.9(9)
Zn(1)–S(2)–P(1)	74.03(6)	S(3)–P(2)–O(4)	112.6(2)	C(2)–C(1)–N(1)	121.9(6)	C(16)–C(15)–C(17)	113.1(6)
Zn(1)–S(3)–P(2)	83.20(6)	S(4)–P(2)–O(4)	107.1(2)				

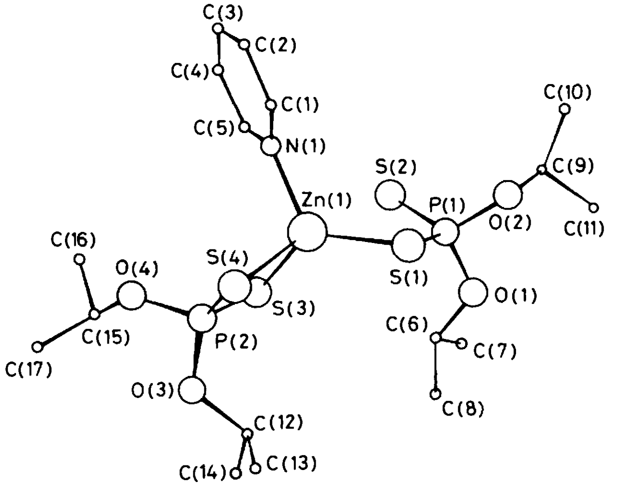

Figure 1. View of the molecule $Zn[S_2P(OPr^i)_2]_2$·py showing the atomic numbering

anisotropic refinement yielded values of 0.07(2) and 0.93(2) for the occupancy factors of S(5) and O(4), respectively, and convergence of a value of 0.0988 for *R*.

Calculations were performed using the CRYSTALS suite of programs,[3] and molecular and unit-cell plots drawn using the PLUTO program.[4] Final fractional atomic co-ordinates are in Tables 3, 5, 7, and 9; intramolecular bond distances and angles are in Tables 4, 6, 8, and 10. Structures with atomic numbering are given in Figures 1—4; the unit-cell contents of [Zn(datau)]-$[S_2P(OEt)_2]_2$ are given in Figure 5.

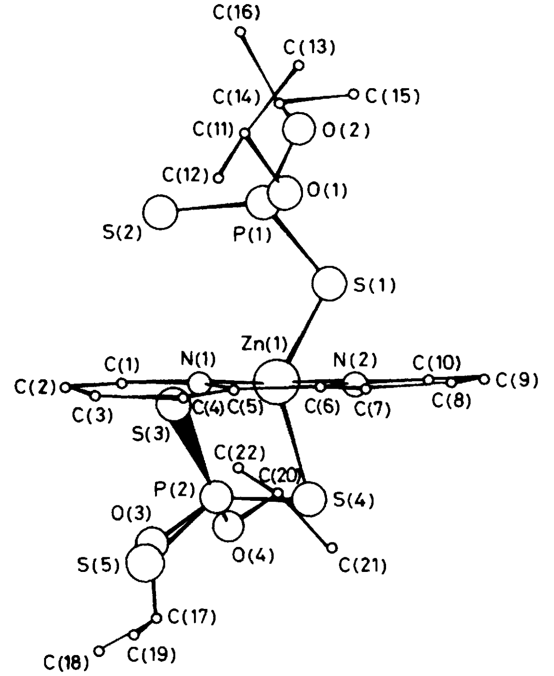

Figure 2. View of the molecule $Zn[S_2P(OPr^i)_2]_2$·bipy showing the atomic numbering

Results and Discussion

Bis(*O,O'*-diethyl- and bis(*O,O'*-di-isopropyl-dithiophosphato)-zinc(II) readily form complexes of 1 : 1 stoicheiometry with a wide range of nitrogen donor ligands [pyridine (py), pyridazine (pydz), ethylenediamine (en), 2,2'-bipyridine (bipy), *N,N'*-diethylethylenediamine (deen), 1,10-phenanthroline (phen), 2,2' : 6',2''-terpyridine (terpy), and 1,11-diamino-3,6,9-triaza-undecane (datau)]. All the complexes are white, crystalline, air-stable solids which exhibit sharp melting points, except for the ethylenediamine complex of $Zn[S_2P(OEt)_2]_2$ which is a viscous liquid at room temperature. Because of the wide range of donor capacity of the ligand employed, and the apparent insensitivity of the principal i.r. bands associated with $S_2P(OR)_2$ (R = alkyl) ligands in these complexes, the structures of four selected complexes, those of pyridine, 2,2'-bipyridine, and 2,2' : 6',2''-terpyridine with $Zn[S_2P(OPr^i)_2]_2$, and the datau complex of $Zn[S_2P(OEt)_2]_2$, were determined.

Structural data have been reported for two zinc(II) bis(*O,O'*-dialkyl dithiophosphates). The *O,O'*-diethyl derivative exhibits a one-dimensional polymeric structure in which one $S_2P(OEt)_2$ ligand chelates each zinc, whilst the second bridges adjacent zinc atoms in the chain.[5] The *O,O'*-di-isopropyl homologue has a dimeric rather than a polymeric structure, but again each zinc is

Table 5. Final fractional atomic co-ordinates for $Zn[S_2P(OPr^i)_2]_2$·bipy with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zn(1)	0.015 6(1)	0.074 9(2)	0.222 1(1)	C(5)	−0.246(2)	0.154(2)	0.267 8(7)
S(1)	0.129 4(4)	−0.140 1(5)	0.263 8(2)	C(6)	−0.314(1)	0.004(2)	0.240 8(7)
S(2)	0.262 3(5)	0.098 7(6)	0.383 4(2)	C(7)	−0.469(2)	−0.069(2)	0.240 8(8)
S(3)	0.282 3(5)	0.301 4(6)	0.220 3(3)	C(8)	−0.522(2)	−0.218(2)	0.217(1)
S(4)	0.016 4(6)	0.147 4(8)	0.111 2(3)	C(9)	−0.420(2)	−0.288(3)	0.190(1)
S(5)	0.140(6)	0.533(4)	0.121(4)	C(10)	−0.267(2)	−0.200(3)	0.193(1)
P(1)	0.143 6(4)	−0.105 9(5)	0.356 2(2)	C(11)	−0.070(2)	−0.134(2)	0.434 3(8)
P(2)	0.198 6(5)	0.325 2(6)	0.132 2(3)	C(12)	−0.195(2)	−0.035(3)	0.421(1)
N(1)	−0.092(1)	0.213(1)	0.268 4(6)	C(13)	−0.115(3)	−0.299(3)	0.467(1)
N(2)	−0.219(1)	−0.060(2)	0.215 7(7)	C(14)	0.362(2)	−0.264(2)	0.410 1(9)
O(1)	−0.031(1)	−0.149(1)	0.370 6(5)	C(15)	0.371(2)	−0.423(3)	0.384(1)
O(2)	0.198(1)	−0.260(1)	0.395 6(5)	C(16)	0.393(2)	−0.266(3)	0.483(1)
O(3)	0.172(2)	0.502(1)	0.128 3(8)	C(17)	0.102(3)	0.579(3)	0.074(1)
O(4)	0.320(1)	0.344(2)	0.083 5(7)	C(18)	0.215(4)	0.735(4)	0.057(1)
C(1)	−0.022(2)	0.349(2)	0.293 5(9)	C(19)	−0.045(3)	0.615(4)	0.094(1)
C(2)	−0.103(3)	0.443(2)	0.321(1)	C(20)	0.391(3)	0.209(3)	0.077(1)
C(3)	−0.259(2)	0.390(3)	0.321(1)	C(21)	0.349(4)	0.174(4)	0.005(2)
C(4)	−0.333(2)	0.248(2)	0.293(1)	C(22)	0.559(3)	0.268(4)	0.096(1)

Table 6. Intermolecular bond distances (Å) and angles (°) for $Zn[S_2P(OPr^i)_2]_2$·bipy with estimated standard deviations in parentheses

Zn(1)–S(1)	2.327(4)	S(5)–P(2)	1.94(1)	N(1)–C(5)	1.36(2)	C(8)–C(9)	1.41(2)
Zn(1)–S(2)	3.822(5)	P(1)–O(1)	1.60(1)	N(2)–C(6)	1.33(2)	C(9)–C(10)	1.41(2)
Zn(1)–S(3)	2.711(4)	P(1)–O(2)	1.60(1)	N(2)–C(10)	1.30(2)	C(11)–C(12)	1.54(2)
Zn(1)–S(4)	2.365(5)	P(2)–O(3)	1.566(9)	C(1)–C(2)	1.42(3)	C(11)–C(13)	1.48(3)
Zn(1)–N(1)	2.09(1)	P(2)–O(4)	1.58(1)	C(2)–C(3)	1.37(3)	C(14)–C(15)	1.55(3)
Zn(1)–N(2)	2.14(1)	O(1)–C(11)	1.47(2)	C(3)–C(4)	1.39(3)	C(14)–C(16)	1.54(3)
S(1)–P(1)	2.005(6)	O(2)–C(14)	1.48(2)	C(4)–C(5)	1.43(2)	C(17)–C(18)	1.52(2)
S(2)–P(1)	1.925(6)	O(3)–C(17)	1.40(2)	C(5)–C(6)	1.43(2)	C(17)–C(19)	1.55(2)
S(3)–P(1)	1.926(9)	O(4)–C(20)	1.47(1)	C(6)–C(7)	1.39(2)	C(20)–C(21)	1.55(4)
S(4)–P(2)	1.997(8)	N(1)–C(1)	1.31(2)	C(7)–C(8)	1.37(2)	C(20)–C(22)	1.50(3)

S(1)–Zn(1)–S(3)	95.4(1)	S(1)–P(1)–O(1)	103.7(4)	Zn(1)–N(1)–C(1)	124(1)	C(6)–C(7)–C(8)	118(1)
S(1)–Zn(1)–S(4)	116.3(1)	S(2)–P(1)–O(1)	115.1(5)	Zn(1)–N(1)–C(5)	114(1)	C(7)–C(8)–C(9)	120(2)
S(1)–Zn(1)–N(1)	129.3(4)	O(1)–P(1)–O(2)	98.8(6)	C(1)–N(1)–C(5)	122(1)	C(8)–C(9)–C(10)	116(2)
S(1)–Zn(1)–N(2)	97.0(4)	S(1)–P(1)–O(2)	106.4(4)	Zn(1)–N(2)–C(6)	115(1)	C(9)–C(10)–N(2)	124(2)
S(3)–Zn(1)–S(4)	79.4(2)	S(2)–P(1)–O(2)	113.3(5)	Zn(1)–N(2)–C(10)	126(1)	O(1)–C(11)–C(12)	105(1)
S(3)–Zn(1)–N(1)	94.5(1)	S(3)–P(2)–O(3)	99.7(7)	C(6)–N(2)–C(10)	119(1)	O(1)–C(11)–C(13)	108(2)
S(3)–Zn(1)–N(2)	167.6(1)	S(4)–P(2)–O(3)	117.5(7)	N(1)–C(1)–C(2)	122(2)	C(12)–C(11)–C(13)	116(2)
S(4)–Zn(1)–N(1)	114.4(1)	S(5)–P(2)–O(3)	7(2)	C(1)–C(2)–C(3)	118(2)	O(2)–C(14)–C(15)	103(1)
S(4)–Zn(1)–N(2)	95.3(1)	O(3)–P(2)–O(4)	102.1(8)	C(2)–C(3)–C(4)	119(2)	O(2)–C(14)–C(16)	104(1)
N(1)–Zn(1)–N(2)	77.4(5)	S(3)–P(2)–O(4)	114.0(6)	C(3)–C(4)–C(5)	120(1)	C(15)–C(14)–C(16)	114(2)
Zn(1)–S(1)–P(1)	97.8(2)	S(4)–P(2)–O(4)	110.9(7)	C(4)–C(5)–C(6)	123(1)	O(3)–C(17)–C(18)	106(2)
Zn(1)–S(3)–P(2)	79.6(2)	S(5)–P(2)–O(4)	104(2)	C(4)–C(5)–N(1)	118(1)	O(3)–C(17)–C(19)	106(2)
Zn(1)–S(4)–P(2)	87.5(3)	P(1)–O(1)–C(11)	120.5(9)	N(1)–C(5)–C(6)	119(1)	C(18)–C(17)–C(19)	111(2)
S(1)–P(1)–S(2)	117.5(3)	P(1)–O(2)–C(24)	122(1)	C(5)–C(6)–C(7)	123(1)	O(4)–C(20)–C(21)	105(2)
S(3)–P(2)–S(4)	112.0(3)	P(2)–O(3)–C(17)	124(1)	C(5)–C(6)–N(2)	115(1)	O(4)–C(20)–C(22)	105(2)
S(3)–P(2)–S(5)	105(2)	P(2)–O(4)–C(20)	120.8(8)	N(1)–C(6)–C(7)	123(1)	C(21)–C(20)–C(22)	115(2)
S(4)–P(2)–S(5)	110(2)						

chelated by one $S_2P(OPr^i)_2$ ligand and the two zinc atoms of the dimer unit bridged by the other $S_2P(OPr^i)_2$ groups.[6] The chelation and bridging is essentially symmetrical and very similar for both compounds, although the Zn–S distances in the bridging system of the isopropyl derivative are significantly lower than those of the ethyl compound (Table 11). In each, the zinc atom has a distorted tetrahedral environment. The principal features of this co-ordination are retained on the formation of the pyridine complex, with one chelating and one essentially unidentate $S_2P(OPr^i)_2$ group and the pyridine nitrogen atom bonded to the metal (Figure 1). The chelation is now, however, distinctly anisobidentate [Zn–S 2.352(2), 2.496(2) Å], although the Zn–S distance of the unidentate $S_2P(OPr^i)_2$ group [2.273(2) Å] is lower than any of the Zn–S distances in dimeric $\{Zn[S_2P(OPr^i)_2]_2\}_2$. The second Zn–S distance for this ligand [3.041(2) Å], although long, is not so long as to preclude some bonding interaction with the zinc, and so the bonding is perhaps best regarded as being highly anisobidentate rather than unidentate in character. The Zn–N distance [2.028(4) Å] is amongst the shortest such observed, being the same within experimental error as that found in bis(*O*-ethyl dithiocarbonato)(pyridine)zinc(II) [2.03(1) Å][7] and [*N*,*N'*-ethylenebis(monothioacetylacetoneiminato)]zinc(II) [2.027(2) Å],[8] and exceeded only by those in dichlorobis(3,5-dimethylpyrazole-N^2)zinc(II) [2.017(3), 2.019(2) Å],[9] [*N*-(2-hydroxyethyl)salicylideneiminato(2−)]zinc(II) [2.007(3) Å],[10] and some of the Zn–N distances in $[(en)_2Zn(C_2O_4)Zn(en)_2]_2I_4$, which range from 1.84(2) to 2.33(2) Å.[11] In contrast, the Zn–N(py) distances in (pyridine)(2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphyrinato)zinc(II) [2.155(3) Å],[12] (2,3-dihydro-5,10,15,20-tetraphenylporphyrinato)(pyridine)zinc(II) [2.171(2) Å],[13] and bis(pyridine)bis[1-(2-thienyl)-4,4,4-trifluorobutane-

Table 7. Final fractional atomic co-ordinates for $Zn[S_2P(OPr^i)_2]_2$·terpy with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zn(1)	0.542 9(2)	0.270 3(1)	0.285 8(1)	C(7)	0.487(2)	0.182 5(6)	0.051(1)
S(1)	0.603 5(5)	0.241 2(1)	0.422 9(2)	C(8)	0.626(2)	0.189 8(7)	0.010(1)
S(2)	0.686 3(5)	0.140 0(2)	0.291 2(3)	C(9)	0.737(2)	0.222 6(7)	0.047(1)
S(3)	0.401 4(4)	0.348 4(1)	0.275 1(3)	C(10)	0.703(2)	0.248 0(6)	0.124 2(8)
S(4)	0.576 7(8)	0.387 1(2)	0.454 9(3)	C(11)	0.810(2)	0.283 4(6)	0.169 9(8)
S(5)	0.614(4)	0.454(1)	0.322(2)	C(12)	0.942(2)	0.302 4(7)	0.135(1)
P(1)	0.614 0(4)	0.162 7(1)	0.400 9(2)	C(13)	1.038(2)	0.332 8(7)	0.183(1)
P(2)	0.465 0(4)	0.404 2(1)	0.355 3(2)	C(14)	0.994(2)	0.346 1(7)	0.265(1)
N(1)	0.337(1)	0.223 8(5)	0.256 8(7)	C(15)	0.859(2)	0.327 4(7)	0.294 7(9)
N(2)	0.574(1)	0.239 6(4)	9.162 2(7)	C(16)	0.421(2)	0.084 5(7)	0.419(1)
N(3)	0.766(1)	0.296 8(5)	0.249 0(7)	C(17)	0.295(3)	0.077(1)	0.357(2)
O(1)	0.451(1)	0.141 6(4)	0.422 4(7)	C(18)	0.378(3)	0.066 6(9)	0.509(2)
O(2)	0.709(1)	0.137 5(4)	0.478 5(6)	C(19)	0.864(2)	0.123 2(6)	0.475(1)
O(3)	0.308(2)	0.430 9(6)	0.372(1)	C(20)	0.878(3)	0.071 0(7)	0.524(2)
O(4)	0.538(3)	0.452 7(6)	0.312(1)	C(21)	0.958(2)	0.167 1(8)	0.517(2)
C(1)	0.213(2)	0.221 0(6)	0.307(1)	C(22)	0.279(3)	0.475(1)	0.432(2)
C(2)	0.082(2)	0.197 9(6)	0.283(1)	C(23)	0.200(4)	0.519(1)	0.384(2)
C(3)	0.071(2)	0.175 9(7)	0.202(1)	C(24)	0.184(5)	0.454(2)	0.500(3)
C(4)	0.198(2)	0.179 1(6)	0.147(1)	C(25)	0.636(4)	0.449(1)	0.238(2)
C(5)	0.326(2)	0.203 0(5)	0.177 8(9)	C(26)	0.777(4)	0.478(1)	0.263(3)
C(6)	0.464(2)	0.208 4(5)	0.127 6(9)	C(27)	0.623(7)	0.505(2)	0.205(4)

Table 8. Intramolecular bond distances (Å) and angles (°) for $Zn[S_2P(OPr^i)_2]_2$·terpy with estimated standard deviations in parentheses

Zn(1)–S(1)	2.334(4)	P(1)–O(1)	1.58(1)	N(3)–C(11)	1.35(2)	C(11)–C(12)	1.38(2)
Zn(1)–S(2)	3.523(5)	P(1)–O(2)	1.61(1)	N(3)–C(15)	1.33(2)	C(12)–C(13)	1.36(2)
Zn(1)–S(3)	2.339(3)	P(2)–O(3)	1.57(1)	C(1)–C(2)	1.34(2)	C(13)–C(14)	1.40(2)
Zn(1)–S(4)	3.977(5)	P(2)–O(4)	1.55(1)	C(2)–C(3)	1.39(3)	C(14)–C(15)	1.37(2)
Zn(1)–N(1)	2.21(1)	O(1)–C(16)	1.47(2)	C(3)–C(4)	1.43(3)	C(16)–C(17)	1.49(3)
Zn(1)–N(2)	2.12(1)	O(2)–C(19)	1.42(2)	C(4)–C(5)	1.37(2)	C(16)–C(18)	1.55(3)
Zn(1)–N(3)	2.17(1)	O(3)–C(22)	1.48(1)	C(5)–C(6)	1.46(2)	C(19)–C(20)	1.53(2)
S(1)–P(1)	2.012(5)	O(4)–C(25)	1.47(1)	C(6)–C(7)	1.40(2)	C(19)–C(21)	1.53(2)
S(2)–P(1)	1.936(5)	N(1)–C(1)	1.36(2)	C(7)–C(8)	1.41(3)	C(22)–C(23)	1.52(4)
S(3)–P(2)	1.968(4)	N(1)–C(5)	1.35(2)	C(8)–C(9)	1.41(3)	C(22)–C(24)	1.48(5)
S(4)–P(2)	1.892(5)	N(2)–C(6)	1.36(2)	C(9)–C(10)	1.41(2)	C(25)–C(26)	1.50(2)
S(5)–P(2)	1.89(1)	N(2)–C(10)	1.31(2)	C(10)–C(11)	1.48(2)	C(25)–C(27)	1.51(2)

S(1)–Zn(1)–S(3)	116.6(1)	S(1)–P(1)–O(2)	106.5(4)	Zn(1)–N(3)–C(11)	116(1)	C(10)–C(11)–C(12)	124(1)
S(1)–Zn(1)–N(1)	101.7(3)	S(2)–P(1)–O(2)	112.7(4)	Zn(1)–N(3)–C(15)	126.3(9)	C(10)–C(11)–N(3)	114(1)
S(1)–Zn(1)–N(2)	134.7(3)	S(3)–P(2)–O(3)	99.5(5)	C(11)–N(3)–C(15)	117(1)	N(3)–C(11)–C(12)	122(1)
S(1)–Zn(1)–N(3)	98.4(3)	S(4)–P(2)–O(3)	114.6(6)	N(1)–C(1)–C(2)	125(1)	C(11)–C(12)–C(13)	120(1)
S(3)–Zn(1)–N(1)	89.6(1)	S(5)–P(2)–O(3)	113(1)	C(1)–C(2)–C(3)	118(2)	C(12)–C(13)–C(14)	118(2)
S(3)–Zn(1)–N(2)	108.5(1)	O(3)–P(2)–O(4)	96(1)	C(2)–C(3)–C(4)	119(2)	C(13)–C(14)–C(15)	119(2)
S(3)–Zn(1)–N(3)	102.1(1)	S(3)–P(2)–O(4)	113.5(8)	C(3)–C(4)–C(5)	118(1)	C(14)–C(15)–N(3)	123(1)
N(1)–Zn(1)–N(2)	74.4(4)	S(4)–P(2)–O(4)	109(1)	C(4)–C(5)–C(6)	123(1)	O(1)–C(16)–C(17)	107(2)
N(1)–Zn(1)–N(3)	149.1(4)	S(5)–P(2)–O(4)	20(2)	C(4)–C(5)–N(1)	123(1)	O(1)–C(16)–C(18)	107(2)
N(2)–Zn(1)–N(3)	74.8(5)	P(1)–O(1)–C(16)	119(1)	N(1)–C(5)–C(6)	114(1)	C(17)–C(16)–C(18)	112(2)
Zn(1)–S(1)–P(1)	99.3(2)	P(1)–O(2)–C(19)	124(1)	C(5)–C(6)–C(7)	124(1)	O(2)–C(19)–C(20)	106(2)
Zn(1)–S(3)–P(2)	114.0(2)	P(2)–O(3)–C(22)	126(1)	C(5)–C(6)–N(2)	116(1)	O(2)–C(19)–C(21)	109(1)
S(1)–P(1)–S(2)	117.4(2)	P(2)–O(4)–C(25)	124(2)	N(2)–C(6)–C(7)	120(1)	C(20)–C(19)–C(21)	111(2)
S(3)–P(2)–S(4)	120.6(3)	Zn(1)–N(1)–C(1)	126(1)	C(6)–C(7)–C(8)	118(2)	O(3)–C(22)–C(23)	108(1)
S(3)–P(2)–S(5)	119(1)	Zn(1)–N(1)–C(5)	116.3(9)	C(7)–C(8)–C(9)	120(1)	O(3)–C(22)–C(24)	108(1)
S(4)–P(2)–S(5)	91(1)	C(1)–N(1)–C(5)	117(1)	C(8)–C(9)–C(10)	118(1)	C(23)–C(22)–C(24)	111(3)
S(1)–P(1)–O(1)	104.5(4)	Zn(1)–N(2)–C(6)	118.6(9)	C(9)–C(10)–C(11)	123(1)	O(4)–C(25)–C(26)	105(2)
S(2)–P(1)–O(1)	113.9(5)	Zn(1)–N(2)–C(10)	119(1)	C(9)–C(10)–N(2)	121(1)	O(4)–C(25)–C(27)	100(2)
O(1)–P(1)–O(2)	100.1(6)	C(6)–N(2)–C(10)	122(1)	N(2)–C(10)–C(11)	115(1)	C(26)–C(25)–C(27)	72(3)

1,3-dionato]zinc(II) [2.128(6), 2.184(11) Å][14] are relatively long. That in the similar complex, $Zn[S_2CNMe_2]_2$·py, is 2.079(6) Å.[15]

Like the pyridine complex (Figure 1), crystals of the homologous 2,2′-bipyridine (Figure 2) and 2,2′:6′,2″-terpyridine (Figure 3) complexes comprise mononuclear species in which both nitrogens of the bipy ligand and all three of terpy are co-ordinated to the zinc. The Zn–N distances are, however, longer than that in the py complex. The co-ordination of bipy is somewhat unsymmetrical [Zn–N 2.09(1), 2.14(1) Å], although the distances fall within the range found for similar complexes such as $ZnCl_2$(bipy) [2.053(2), 2.064(2) Å],[16] $[Zn(ONO)(bipy)_2]NO_3$ [2.076(9), 2.129(9) Å],[17] $[(bipy)ZnFe(CO)_4]_2$ [2.116(2), 2.117(2) Å],[18] and $[Zn(H_2ATP)(bipy)]_2$·$4H_2O$ [H_2ATP = adenosine 5′-triphosphate(2−)] [2.13(3), 2.14(4) Å].[19] The Zn–N distances in the terpy complex are longer still [2.17(1), 2.12(1), 2.21(1) Å], the shortest distance being to the central nitrogen atom, a feature which is also observed in $ZnCl_2$(terpy) [Zn–N 2.18(4), 2.09(4), 2.24(4) Å].[20]

The extra co-ordination provided by these donor ligands has

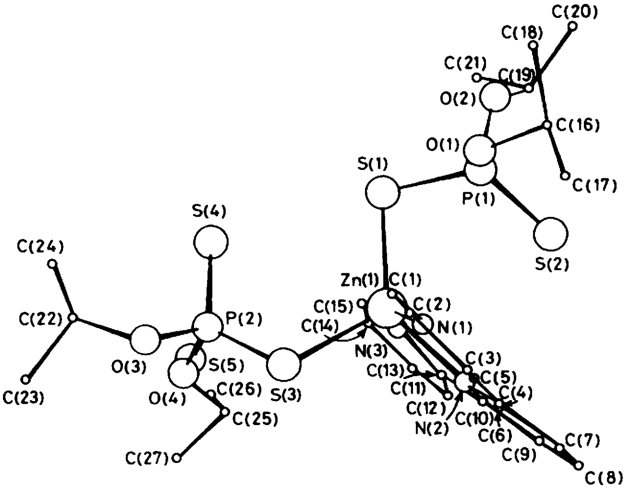

Figure 3. View of the molecule Zn[$S_2P(OPr^i)_2$]$_2$·terpy showing the atomic numbering

a profound effect upon the mode of bonding of the $S_2P(OPr^i)_2$ groups to the zinc. Whereas in the py complex one $S_2P(OPr^i)_2$ group chelates unsymmetrically and the other is unidentate, replacement of py by bipy causes the anisobidentate character of the chelating $S_2P(OPr^i)_2$ ligand to become much more pronounced, whilst with terpy, both $S_2P(OPr^i)_2$ groups are unidentate (Table 11). This trend is seen to reach its ultimate in the complex of Zn[$S_2P(OEt)_2$]$_2$ with datau, in which both $S_2P(OEt)_2$ groups are ionised from the zinc and the closest Zn···S contact is 4.153(3) Å (Figures 4 and 5). The zinc(II) cation is co-ordinated by all five nitrogen atoms of the pentamine ligand in a distorted trigonal-bipyramidal fashion, and is therefore chiral in the solid. The three 'equatorial' Zn–N distances [2.047(6), 2.053(6), 2.090(6) Å] are significantly shorter than the two 'axial' Zn–N distances [2.166(6), 2.191(6) Å], and the sum of the N_{eq}–Zn–N_{eq} bond angles [126.8(3), 117.4(3), 115.5(3)°] is 359.7° (the zinc lies only 0.063 Å out of the plane defined by the three equatorial nitrogen atoms). The N_{ax}–Zn–N_{ax} bond angle deviates from linearity by only a small degree [161.3(3)°]. The only other example of displacement of $S_2P(OR)_2$ groups from a metal as $S_2P(OR)_2^-$ anions, of

Table 9. Final fractional atomic co-ordinates for [Zn(datau)][$S_2P(OEt_2)_2$]$_2$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Zn(1)	0.180 7(1)	0.346 45(3)	0.460 67(6)	C(1)	0.173(1)	0.439 3(4)	0.347 3(7)
S(1)	−0.030 1(4)	0.415 8(1)	0.692 3(2)	C(2)	0.118(1)	0.461 2(3)	0.431 5(7)
S(2)	0.134 3(4)	0.295 3(1)	0.739 6(2)	C(3)	0.366(1)	0.440 3(3)	0.547 4(6)
S(3)	0.684 8(3)	0.403 3(1)	0.399 7(1)	C(4)	0.445(1)	0.390 9(4)	0.594 5(6)
S(4)	0.453 8(3)	0.318 0(1)	0.255 8(2)	C(5)	0.469(1)	0.293 5(3)	0.563 6(6)
P(1)	0.040 5(3)	0.359 99(9)	0.781 3(1)	C(6)	0.412(1)	0.254 0(4)	0.487 9(6)
P(2)	0.604 1(3)	0.377 90(9)	0.276 3(1)	C(7)	0.117(1)	0.235 3(3)	0.503 2(6)
N(1)	0.127 7(8)	0.381 3(3)	0.335 6(4)	C(8)	−0.048(1)	0.263 4(4)	0.488 0(7)
N(2)	0.187 1(8)	0.428 4(2)	0.510 7(5)	C(9)	−0.263(1)	0.327 0(6)	0.790 6(8)
N(3)	0.427 4(7)	0.347 8(3)	0.526 0(4)	C(10)	−0.384(1)	0.333 6(6)	0.854(1)
N(4)	0.232 4(9)	0.262 4(2)	0.451 2(4)	C(11)	0.135(2)	0.427 6(5)	0.915(1)
N(5)	−0.020 6(8)	0.320 2(3)	0.513 4(4)	C(12)	0.280(3)	0.432 0(9)	0.995(1)
O(1)	−0.103 0(7)	0.346 0(2)	0.836 3(3)	C(13)	0.605(2)	0.475 9(5)	0.214(1)
O(2)	0.172 8(8)	0.380 6(3)	0.864 4(4)	C(14)	0.478(2)	0.518 5(5)	0.200(1)
O(3)	0.515 6(8)	0.425 5(3)	0.216 9(4)	C(15)	0.756(2)	0.349 1(6)	0.140 2(8)
O(4)	0.770 4(7)	0.367 9(3)	0.234 7(4)	C(16)	0.887(2)	0.373 6(6)	0.099 8(9)

Table 10. Intraionic bond distances (Å) and angles (°) for [Zn(datau)][$S_2P(OEt_2)_2$]$_2$ with estimated standard deviations in parentheses

Zn(1)–N(1)	2.047(6)	S(2)–P(1)	1.948(3)	O(3)–C(13)	1.47(1)	N(5)–C(8)	1.49(1)
Zn(1)–N(2)	2.191(6)	S(3)–P(2)	1.962(3)	O(4)–C(15)	1.48(1)	C(1)–C(2)	1.51(1)
Zn(1)–N(3)	2.090(6)	S(4)–P(2)	1.938(3)	N(1)–C(1)	1.51(1)	C(3)–C(4)	1.52(1)
Zn(1)–N(4)	2.166(6)	P(1)–O(1)	1.584(6)	N(2)–C(2)	1.48(1)	C(5)–C(6)	1.52(1)
Zn(1)–N(5)	2.053(6)	P(1)–O(2)	1.593(7)	N(2)–C(3)	1.50(1)	C(7)–C(8)	1.51(1)
Zn(1)···S(1)	4.481(3)	P(2)–O(3)	1.591(6)	N(3)–C(4)	1.48(1)	C(9)–C(10)	1.49(2)
Zn(1)···S(2)	4.449(3)	P(2)–O(4)	1.609(6)	N(3)–C(5)	1.50(1)	C(11)–C(12)	1.55(2)
Zn(1)···S(3)	4.253(2)	O(1)–C(9)	1.45(1)	N(4)–C(6)	1.50(1)	C(13)–C(14)	1.48(2)
Zn(1)···S(4)	4.153(3)	O(2)–C(11)	1.47(2)	N(4)–C(7)	1.49(1)	C(15)–C(16)	1.46(2)
S(1)–P(1)	1.956(3)						
N(1)–Zn(1)–N(2)	84.2(3)	S(2)–P(1)–O(1)	110.4(3)	P(2)–O(4)–C(15)	118.8(6)	N(1)–C(1)–C(2)	110.3(7)
N(1)–Zn(1)–N(3)	117.4(3)	O(1)–P(1)–O(2)	97.6(3)	Zn(1)–N(1)–C(1)	107.3(5)	N(2)–C(2)–C(1)	110.0(7)
N(1)–Zn(1)–N(4)	111.8(3)	S(1)–P(1)–O(2)	112.5(3)	Zn(1)–N(2)–C(2)	105.5(5)	N(2)–C(3)–C(4)	108.4(7)
N(1)–Zn(1)–N(5)	115.5(3)	S(2)–P(1)–O(2)	105.7(3)	Zn(1)–N(2)–C(3)	106.2(5)	N(3)–C(4)–C(3)	107.1(7)
N(2)–Zn(1)–N(3)	81.9(3)	S(3)–P(2)–O(3)	109.4(3)	C(2)–N(2)–C(3)	113.4(6)	N(3)–C(5)–C(6)	107.2(7)
N(2)–Zn(1)–N(4)	161.3(3)	S(4)–P(2)–O(3)	106.3(3)	Zn(1)–N(3)–C(4)	107.9(5)	N(4)–C(6)–C(5)	109.7(7)
N(2)–Zn(1)–N(5)	98.4(2)	O(3)–P(2)–O(4)	103.7(4)	Zn(1)–N(3)–C(5)	107.6(5)	N(4)–C(7)–C(8)	109.6(7)
N(3)–Zn(1)–N(4)	82.1(3)	S(3)–P(2)–O(4)	104.1(3)	C(4)–N(3)–C(5)	114.7(6)	N(5)–C(8)–C(7)	108.7(7)
N(3)–Zn(1)–N(5)	126.8(3)	S(4)–P(2)–O(4)	111.9(3)	Zn(1)–N(4)–C(6)	107.7(5)	O(1)–C(9)–C(10)	108(1)
N(4)–Zn(1)–N(5)	83.6(3)	P(1)–O(1)–C(9)	121.1(6)	Zn(1)–N(4)–C(7)	105.4(5)	O(2)–C(11)–C(12)	105(1)
S(1)–P(1)–S(2)	118.0(2)	P(1)–O(2)–C(11)	119.4(8)	C(6)–N(4)–C(7)	114.4(7)	O(3)–C(13)–C(14)	107(1)
S(3)–P(2)–S(4)	120.4(2)	P(2)–O(3)–C(13)	119.0(7)	Zn(1)–N(5)–C(8)	107.9(5)	O(4)–C(15)–C(16)	108.4(9)
S(1)–P(1)–O(1)	110.8(3)						

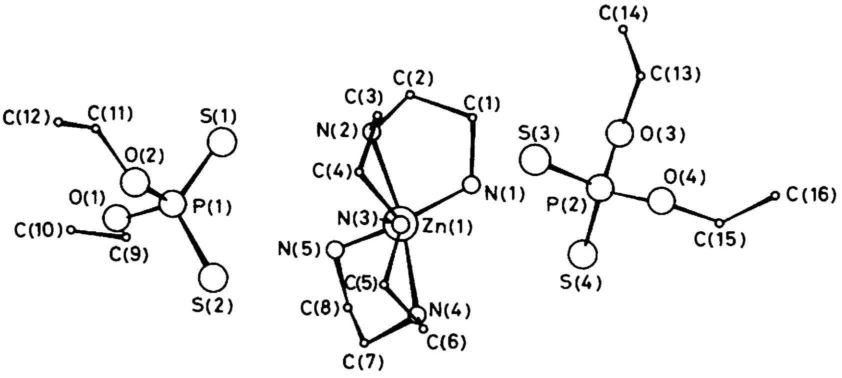

Figure 4. View of the cation and anions in the complex [Zn(datau)][$S_2P(OEt)_2$]$_2$ showing the atomic numbering

Table 11. Comparative structural data for complexes Zn[$S_2P(OPr^i)_2$]$_2$·L (L = py, bipy, or terpy), [Zn(datau)][$S_2P(OEt)_2$]$_2$, and related compounds

Compound	M–S (Å)	P–S (Å)	$\widehat{\text{M–S–P}}$ (°)	$\widehat{\text{S–P–S}}$ (°)	$\widehat{\text{S–M–S}}$ (°)	P–O (Å)	$\widehat{\text{O–P–O}}$ (°)	Ref.
{Zn[$S_2P(OEt)_2$]$_2$}$_n$								
Chelating	2.315(6), 2.401(7)	1.987(9), 1.97(1)	82.5(3), 81.5(3)	109.7(4)	85.9(2)	1.56(2), 1.62(2)	95(1)	*a*
Bridging	2.345(4), 2.337(7)	1.992(7), 2.001(5)	101.8(2), 106.4(3)	108.0(3)		1.57(1), 1.57(1)	97.4(7)	
{Zn[$S_2P(OPr^i)_2$]$_2$}$_2$								
Chelating	2.351(5), 2.409(5)	1.984(7), 1.968(7)	82.6(2), 81.4(2)	109.7(3)	85.5(2)	1.56(1), 1.57(1)	94.9(8)	*b*
Bridging	2.306(5), 2.302(6)	1.957(7), 1.971(7)	100.6(2), 104.1(2)	117.3(3)		1.60(1), 1.58(2)	104.4(8)	
Zn[$S_2P(OPr^i)_2$]$_2$·py								
Chelating	2.352(2), 2.496(2)	2.007(2), 1.971(2)	83.20(6), 80.20(6)	110.95(8)	85.03(5)	1.573(4), 1.566(4)	101.4(2)	*c*
Unidentate	2.273(2)	2.010(2), 1.948(2)	93.63(7)	113.82(9)		1.579(4), 1.579(4)	100.3(2)	
Zn[$S_2P(OPr^i)_2$]$_2$·bipy								
Chelating	2.711(4), 2.365(5)	1.926(9), 1.997(8)	79.6(2), 87.5(3)	112.0(3)	79.4(2)	1.566(9), 1.58(1)	102.1(8)	*c*
Unidentate	2.327(4)	2.005(6), 1.925(6)	97.8(2)	117.5(3)		1.60(1), 1.60(1)	98.8(6)	
Zn[$S_2P(OPr^i)_2$]$_2$·terpy								
Unidentate: ligand 1	2.334(4)	2.012(5), 1.936(5)	99.3(2)	117.4(2)		1.58(1), 1.61(1)	100.1(6)	
Unidentate: ligand 2	2.339(3)	1.968(4), 1.892(5)	114.0(2)	120.6(3)		1.57(1), 1.55(1)	96(1)	*c*
[Zn(datau)][$S_2P(OEt)_2$]$_2$								
Ionic: anion 1		1.962(3), 1.938(3)		120.4(2)		1.591(6), 1.609(6)	103.7(4)	
Ionic: anion 2		1.956(3), 1.948(3)		118.0(2)		1.584(6), 1.593(7)	97.6(3)	*c*
Zn_4[$S_2P(OEt)_2$]$_6$S								
Bridging: ligand 1	2.335(3), 2.337(3)	1.983(5), 1.993(5)	109.9(2), 106.6(2)	120.5(2)		1.60(1), 1.568(9)	101.6(5)	
Bridging: ligand 2	2.353(4), 2.341(4)	1.981(6), 1.968(6)	106.6(2), 108.5(2)	121.1(2)		1.53(1), 1.56(2)	100(1)	*d*
[Zn(S_2PEt_2)$_2$]$_2$								
Dimer A								*e*
Chelating: ligand 1	2.40(1), 2.454(7)	1.996(8), 2.05(1)	82.7(4), 80.3(3)	110.3(5)	86.3(3)			
Chelating: ligand 2	2.416(8), 2.368(7)	2.01(1), 2.00(1)	81.8(4), 83.3(4)	108.7(5)	86.0(3)			
Bridging: ligand 3	2.302(7), 2.382(9)	2.006(8), 2.027(9)	102.1(3), 105.1(4)	116.7(3)				
Bridging: ligand 4	2.341(9), 2.339(9)	2.05(1), 1.998(9)	105.1(4), 99.2(5)	115.3(4)				
Dimer B								
Chelating: ligand 1	2.370(7), 2.509(8)	2.04(1), 1.985(7)	83.3(3), 80.9(3)	110.4(5)	85.3(3)			
Chelating: ligand 2	2.46(1), 2.378(7)	2.00(1), 2.06(2)	81.8(4), 82.7(4)	109.0(6)	86.1(3)			
Bridging: ligand 3	2.332(8), 2.325(6)	2.06(1), 1.990(9)	102.7(3), 106.6(3)	115.5(5)				
Bridging: ligand 4	2.313(6), 2.321(6)	2.00(1), 2.06(1)	104.0(4), 102.5(4)	115.3(5)				
[Zn($S_2PPr^n{}_2$)$_2$]$_2$								
Chelating	2.45(1), 2.344(2)	2.07(1), 2.011(2)	78.8(6), 82.7(1)	109.8(6)	88.4(5)			*f*
Bridging	2.306(2), 2.321(2)	2.005(2), 2.002(2)	104.6(3), 105.6(3)	118.2(3)				
[Zn(S_2PPh_2)$_3$]$^-$								
Chelating	2.449(2), 2.453(2)	2.005(3), 2.001(3)	82.85(9), 82.83(9)	110.0(1)	84.01(7)			*g*
Unidentate: ligand 1	2.305(2)	2.053(3), 1.951(3)	100.2(1)	117.0(1)				
Unidentate: ligand 2	2.306(2)	2.030(3), 1.961(3)	100.2(1)	114.3(1)				
[Zn{$S_2P(OC_6H_4Me$-*p*)$_2$}$_3$]								
Chelating	2.423(4), 2.423(4)	1.978(5), 1.961(5)	80.5(2), 80.8(2)	113.2(2)	85.5(1)	1.621(9), 1.579(9)	103.7(5)	*g*
Unidentate: ligand 1	2.308(4)	1.986(6), 1.921(5)	102.3(2)	119.1(3)		1.58(1), 1.611(9)	99.2(5)	
Unidentate: ligand 2	2.296(4)	1.987(5), 1.927(5)	100.6(2)	100.6(3)		1.601(9), 1.594(9)	100.4(5)	

[a] Ref. 5. [b] Ref. 6. [c] This work. [d] Preceding paper (ref. 1). [e] M. Calligaris, G. Nardin, and A. Ripamonti, *J. Chem. Soc. A*, 1970, 714. [f] H. Wunderlich, *Acta Crystallogr., Sect. B*, 1982, **38**, 614. [g] J. A. McCleverty, R. S. Z. Kowalski, N. A. Bailey, R. Mulvaney, and D. A. O'Cleirigh, *J. Chem. Soc., Dalton Trans.*, 1983, 627.

which we are aware, is with bis(*O,O′*-dimethyl dithiophosphato)nickel(II), which with >3 mol equiv. of 1,10-phenanthroline in acetone or ethanol affords the ionic complex [Ni(phen)$_2$][$S_2P(OMe)_2$]$_2$.[21]

Examination of the data in Table 11 shows that the geometry of the $S_2P(OR)_2$ ligand framework varies somewhat on change in co-ordination. Ranges of both the P–S and P–O bond distances are quite small [P–S 1.892(5)—2.07(1) Å, P–O

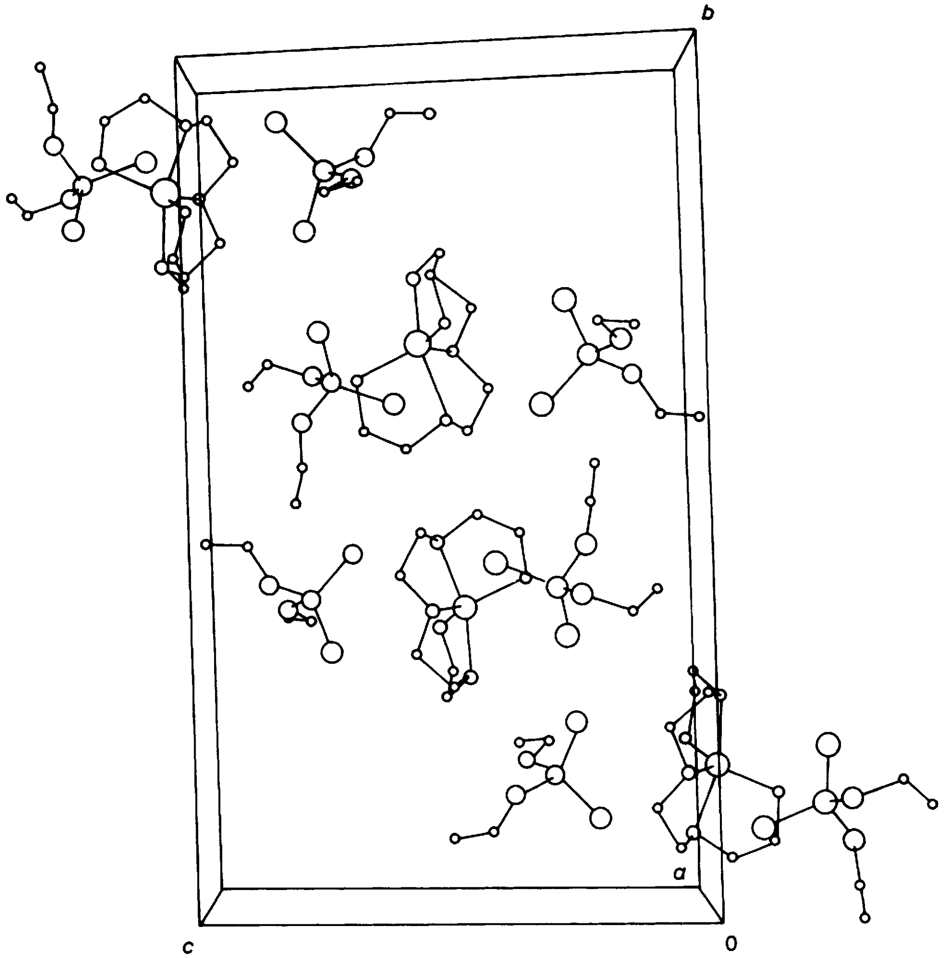

Figure 5. View of the unit-cell contents of $[Zn(datau)][S_2P(OEt)_2]_2$

Table 12. Selected i.r. data (cm^{-1})[a]

Compound	ν[(P)–O–C]	ν[P–O–(C)]	$\nu_{asym}(PS_2)$	$\nu_{sym}(PS_2)$
$Zn[S_2P(OEt)_2]_2$	1 161m, 1 105m	1 013s, 974s,br	655s,d, 640s	542m, 525m,d
$Zn[S_2P(OEt)_2]_2\cdot py$	1 161m,br, 1 099m	1 015s, 948s,br	650s, 641s,d	546s,br
$Zn[S_2P(OEt)_2]_2\cdot pydz$	1 160s, 1 096s	1 018s,br, 951s,br	667s,br	550s,br
$Zn[S_2P(OEt)_2]_2\cdot en$[b]	1 158m, 1 096s	1 025s, 947s	667s	532m, 516m
$Zn[S_2P(OEt)_2]_2\cdot bipy$	1 156m, 1 096m	1 016s, 943s	667s	542m,br
$Zn[S_2P(OEt)_2]_2\cdot deen$	1 153m, 1 096s	1 016s,br, 952s,br	672s	548s, 525m
$Zn[S_2P(OEt)_2]_2\cdot phen$	1 161m,br, 1 103m	1 021s,br, 949s,br	659s,br	556m,br
$Zn[S_2P(OEt)_2]_2\cdot terpy$	1 162m, 1 098m,br	1 026s, 944s	656s	555m,br
$[Zn(datau)][S_2P(OEt)_2]_2$	1 159m, 1 094s	1 027s,br, 934s,br	673s,br	556m, 530m
$Zn_4[S_2P(OEt)_2]_6O$	1 159m,br, 1 100m	1 016s,br, 956s,br	667s, 650s,d	541s
$Zn_4[S_2P(OEt)_2]_6S$	1 156m,br, 1 100m	1 016s,br, 955s,br	656s, 638s,d	535s,br
$HS(S)P(OEt)_2$[b]	1 160m, 1 098m	1 015s, 963s	655s	543m,d, 511m
$Zn[S_2P(OPr^i)_2]_2$	1 179s, 1 142s, 1 103s	973s,br	652s,br	535s
$Zn[S_2P(OPr^i)_2]_2\cdot py$	1 178m, 1 140m, 1 104s	991s, 996s	662s, 648s,d	551s
$Zn[S_2P(OPr^i)_2]_2\cdot pydz$	1 178m, 1 140m, 1 103m	970s,br	667s	557m, 542m,d
$Zn[S_2P(OPr^i)_2]_2\cdot en$	1 178s, 1 139s, 1 109s,br	1 028s, 964s,br	667s,br	556s, 517m
$Zn[S_2P(OPr^i)_2]_2\cdot bipy$	1 171m, 1 143m,br, 1 017m	988s, 956s	667s	559m, 549m
$Zn[S_2P(OPr^i)_2]_2\cdot deen$	1 181s, 1 141s, 1 110s	970s,br	669s, 653s	554s,d, 536s
$Zn[S_2P(OPr^i)_2]_2\cdot phen$	1 177m, 1 141m,br, 1 108m	989s,d, 960s	677s, 666s,d	540s
$Zn[S_2P(OPr^i)_2]_2\cdot terpy$	1 178m, 1 140m, 1 109m	987s,d, 954s	667s	562m
$Zn_4[S_2P(OPr^i)_2]_6O$	1 178s, 1 139s, 1 105s	983s,br	667s, 651s,d	543s
$[S_2P(OPr^i)_2]_2$	1 183m, 1 144m, 1 105m	1 020s,d, 972s,br	636s	499s

[a] Recorded as KBr discs using a PE683 spectrophotometer; m = medium; s = strong; br = broad; d = less intense peak doublet. [b] Recorded as liquid films.

1.53(1)—1.62(2) Å]. Symmetrically chelating or symmetrically bridging $S_2P(OR)_2$ ligands exhibit equal or very nearly equal P–S bond distances [Δ(P–S) < 0.02 Å], which correspond to Zn–S bond distances of similar magnitude [Δ(Zn–S) < 0.05 Å]. However, the greater the anisobidentate character of the chelation, the more pronounced becomes the difference in length of the two P–S distances within the $S_2P(OR)_2$ ligand, as they assume, respectively, P–S single and P=S double bond character. Thus, for $Zn[S_2P(OPr^i)_2]_2$·py, the two P–S distances of the unidentate $S_2P(OPr^i)_2$ group are 1.948(2) and 2.010(2) Å [Δ(P–S) 0.062, Δ(Zn–S) 0.768 Å]. The corresponding data for $Zn[S_2P(OPr^i)_2]_2$·bipy are: P–S 1.926(9), 1.997(8) Å [Δ(P–S) 0.029, Δ(Zn–S) 0.346 Å] for the anisobidentate ligand, and P–S 1.925(6), 2.005(6) Å [Δ(P–S) 0.080, Δ(Zn–S) 1.495 Å] for the unidentate ligand; for the two unidentate $S_2P(OPr^i)_2$ ligands of $Zn[S_2P(OPr^i)_2]_2$·terpy: ligand 1, P–S 1.936(5), 2.012(5) Å [Δ(P–S) 0.076 Å, Δ(Zn–S) 1.189 Å]; ligand 2, P–S 1.892(5), 1.968(4) Å [Δ(P–S) 0.076 Å, Δ(Zn–S) 1.638 Å]. *A priori*, it might be expected that both P–S distances in the $S_2P(OEt)_2^-$ anions would be equal; however, this is not observed, and both anions exhibit some degree of P–S inequality [anion 1, 1.938(3), 1.962(3) Å; anion 2, 1.948(3), 1.956(3) Å]. The SPS bond angle also varies with the nature of the ligand co-ordination. Symmetrically chelating ligands exhibit angles of *ca.* 110°, whereas that in the anisobidentate ligand of the bipy complex is 112.0°. In the unidentate group of the py complex it is increased to 113.8°, but in the bipy and terpy complexes values of 117.5, 117.4, and 120.6° are observed. Similar values (118.0, 120.4°) are exhibited by the $S_2P(OEt)_2^-$ anions of [Zn(datau)]-$[S_2P(OEt)_2]_2$ and by the bridging ligands in $Zn_4[S_2P(OEt)_2]_6S$ (120.5, 121.1°)[1] and $\{Zn[S_2P(OPr^i)_2]_2\}_2$,[6] but that associated with the bridging ligand in $\{Zn[S_2P(OEt)_2]_2\}_n$ is much lower (108.0°).[5] Variations are also observed in both the P–O bond distances and the OPO angles, although these are of a much less systematic nature.

Table 12 lists the principal i.r. vibrations associated with the *O,O′*-dialkyl dithiophosphate skeleton for the complexes and related compounds. The $\nu_{asym}(PS_2)$ and $\nu_{sym}(PS_2)$ vibrations appear quite insensitive to the variation in the environment of the $S_2P(OR)_2$ group, and fall in the narrow ranges of 636—677 and 511—562 cm^{-1}, respectively. The ν[P–O–(C)] vibration is usually strong and broad. For the $S_2P(OEt)_2$ derivatives two bands are observed at 943—974 and 1 013—1 027 cm^{-1}, whereas the isopropyl analogues exhibit one or two bands in the range 954—1 028 cm^{-1}. For the corresponding ν[(P)–O–C] vibration, two (in the case of the ethyl derivatives) or three (for the isopropyl derivatives) sharper though weaker bands are observed in the range 1 094—1 183 cm^{-1}. Infrared is, therefore, not a useful probe for the determination of the nature of the bonding of $S_2P(OR)_2$ groups.

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