Complexes of Lead(II) Bis(*O,O'*-dialkyl dithiophosphates) with Nitrogen Donor Ligands. The Crystal Structures of $Pb[S_2P(OEt)_2]_2$·en (en = ethylenedianine), $Pb[S_2P(OEt)_2]_2$·bipy (bipy = 2,2'-bipyridine), and $\{Pb[S_2P(OEt)_2]_2\}_2$·en†

Philip G. Harrison,* Michael G. Begley, Thakor Kikabhai, and Andrew T. Steel
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD
Mutasim I. Khalil
Department of Chemistry, King Saud University, Riyadh, Saudi Arabia

Ten complexes of lead(II) bis(*O,O'*-dialkyl dithiophosphates) with nitrogen donor molecules of the type $Pb[S_2P(OR)_2]_2$·L [R = Et or Pr^i; L = ethylenediamine (en), 2,2'-bipyridine (bipy), *N,N'*-diethylethylenediamine (deen), 1,10-phenanthroline (phen), or 2,2';6',2''-terpyridine (terpy)] have been prepared by mixing the components in a 1:1 molar ratio in ethanol–dichloromethane (1:1). Mixing en with $Pb[S_2P(OEt)_2]_2$ in a 1:1 molar ratio in xylene affords the complex $\{Pb[S_2P(OEt)_2]_2\}_2$·en. The crystal structures of three of the complexes, $Pb[S_2P(OEt)_2]_2$·en (**1**), $Pb[S_2P(OEt)_2]_2$·bipy (**2**), and $\{Pb[S_2P(OEt)_2]_2\}_2$·en (**3**) have been determined by the heavy-atom method from diffractometer data using Mo-K_α radiation (λ = 0.7107 Å). Crystal data: (**1**) monoclinic, space group $P2_1/c$, with a = 14.727(2), b = 14.490(2), c = 11.616(2) Å, β = 110.72(2)°, and Z = 4; (**2**) triclinic, space group $P\bar{1}$, with a = 10.933(2), b = 13.257(2), c = 13.705(2) Å, α = 103.58(2), β = 132.24(2), γ = 91.50(2)°, and Z = 2; (**3**) triclinic, space group $P\bar{1}$, with a = 9.997(2), b = 14.875(2), c = 15.000(2) Å, α = 98.54(2), β = 100.77(2), γ = 95.64(2)°, and Z = 2. Crystals of (**2**) comprise discrete centrosymmetric dimer molecules, the central feature of which is a rectangular four-membered Pb_2S_2 ring. Both en complexes (**1**) and (**3**) exhibit polymeric structures.

The interaction of amines with lead(II) bis(*O,O'*-dialkyl dithiophosphates), $Pb[S_2P(OR)_2]_2$, is intriguing. Xylene solutions containing simple amines such as mono-, di-, and triethylamine and $Pb[S_2P(OEt)_2]_2$ (R = Et or Pr^i) over a period of 12—24 h slowly become orange and darken to give very dark red solutions from which very fine precipitates of lead(II) sulphide are deposited. *A priori*, decomposition of lead(II) bis(*O,O'*-dialkyl dithiophosphates) in the presence of amines could take place by attack of the nitrogenous base at either the lead, sulphur, or phosphorus centres. Although the reaction pathway by which base-induced elimination of lead sulphide occurs must be quite complex, little insight as to the course of these reaction could be obtained from either i.r., u.v., or ^{207}Pb and ^{31}P n.m.r. spectra. Nevertheless, we have been able to isolate complexes of lead(II) bis(*O,O'*-dialkyl dithiophosphates) with several bidentate nitrogen donor molecules, and an examination of the structures of three of these by *X*-ray crystallography which are reported herein, indicates that the initial interaction with amines is at the metal centre.

Experimental

Synthesis of the Complexes.—The lead(II) bis(*O,O'*-dialkyl dithiophosphates) were synthesized as described previously.[1] The complexes with nitrogen donor ligands were obtained by treating the lead(II) bis(*O,O'*-dialkyl dithiophosphate) (4×10^{-4} mol) dissolved in the minimum volume of ethanol–dichloromethane (1:1, v/v) with an equimolecular quantity of the appropriate amine. Liquid amines were added directly, but solid amines were dissolved in the minimum volume of ethanol before addition to lead(II) bis(*O,O'*-dialkyl dithiophosphate) solutions. The mixtures were allowed to stand overnight at room temperature, after which the products were filtered off and recrystallized from hot ethanol. The complex $\{Pb[S_2P(OEt)_2]_2\}_2$·en (en = ethylenediamine) was similarly obtained by mixing the two components in xylene. Physical and microanalytical data are collected in Table 1.

Structure Determinations of $\{Pb[S_2P(OEt)_2]_2\}_2$·en (**3**), $Pb[S_2P(OEt)_2]_2$·en (**1**), *and* $Pb[S_2P(OEt)_2]_2$·bipy (**2**; bipy = 2,2'-bipyridine).—The same crystallographic methods were applied in the determination of all three structures and the crystal data are collected in Table 2. Approximate cell dimensions and the space groups were determined from oscillation and first- and second-layer Weissenberg photographs. Accurate cell dimensions were obtained from a least-squares refinement of *ca.* 23 reflections using a Hilger and Watts four-circle diffractometer, which was also used to measure the intensities of independent reflections in the range $0 < \theta < 25°$, with reflections showing $I < 3\sigma(I)$ being considered unobserved. Lorentz, polarization, and absorbance corrections were applied. Calculations were performed using the CRYSTALS[2] suite of programs. Atomic scattering factors for all atoms were obtained from ref. 3, with real and imaginary dispersion corrections being made for lead, sulphur, and phosphorus. Molecular drawings were performed using the PLUTO plotting program.[4] The approximate position of the lead atoms was obtained from three-dimensional Patterson syntheses. The positions of the other non-hydrogen light atoms were located by a series of three-dimensional Fourier and Fourier difference syntheses. A weighting scheme was applied only in the case of $Pb[S_2P(OEt)_2]_2$·en, which was of the form

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

where the terms $A(I)$ (I = 0—3) are the coefficients of a Chebyshev series in $T(I)'(\chi)$ [$\chi = F_o/F_o(\text{max.})$]. Final fractional atomic co-ordinates, anisotropic thermal parameters, and interatomic distances and angles for $\{Pb[S_2P(OEt)_2]_2\}_2$·en (**3**) are listed in Tables 3 and 4, those for $Pb[S_2P(OEt)_2]_2$·en (**1**) in Tables 5 and 6, and those for $Pb[S_2P(OEt)_2]_2$·bipy (**2**) in Tables 7 and 8.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvi–xx.

Table 1. Physical and microanalytical[a] data

Compound/Complex[b]	Colour	M.p. (°C)	Analysis (%) C	H	N
$Pb[S_2P(OEt)_2]_2$	White	76—77	16.45 (16.65)	3.60 (3.50)	
$Pb[S_2P(OEt)_2]_2$•0.5en[c]	Colourless	80—82	18.75 (18.85)	4.00 (3.95)	2.30 (2.30)
$Pb[S_2P(OEt)_2]_2$•en	White	93—95	18.90 (18.85)	4.40 (4.45)	3.90 (4.40)
$Pb[S_2P(OEt)_2]_2$•bipy	Pale green	116—117	29.50 (29.45)	4.00 (3.85)	4.05 (3.80)
$Pb[S_2P(OEt)_2]_2$•deen	White	105—106	24.30 (24.25)	5.30 (5.25)	4.05 (4.05)
$Pb[S_2P(OEt)_2]_2$•phen	White	114—116	32.00 (31.70)	3.75 (3.70)	3.80 (3.70)
$Pb[S_2P(OEt)_2]_2$•terpy	Yellow	139—140	34.45 (34.05)	4.00 (3.85)	5.20 (5.20)
$Pb[S_2P(OPr^i)_2]_2$	White	126—128	22.65 (22.75)	4.55 (4.45)	
$Pb[S_2P(OPr^i)_2]_2$•en	White	82—84	24.05 (24.25)	5.25 (5.25)	3.75 (4.05)
$Pb[S_2P(OPr^i)_2]_2$•bipy	Pale yellow	102—104	33.60 (33.45)	4.65 (4.60)	3.75 (3.55)
$Pb[S_2P(OPr^i)_2]_2$•deen	White	118—119	29.00 (28.85)	6.05 (5.90)	3.75 (3.75)
$Pb[S_2P(OPr^i)_2]_2$•phen	Pale green	152—154	35.05 (34.40)	4.65 (4.45)	3.60 (3.45)
$Pb[S_2P(OPr^i)_2]_2$•terpy	Yellow	148—150	37.40 (37.40)	4.65 (4.55)	5.35 (4.85)

[a] Calculated values are given in parentheses. [b] deen = *N,N'*-diethylethylenediamine, phen = 1,10-phenanthroline, terpy = 2,2'; 6',2''-terpyridine. [c] Pb 34.7 (34.5%).

Table 2. Crystal data for $\{Pb[S_2P(OEt)_2]_2\}_2$•en (**3**), $Pb[S_2P(OEt)_2]_2$•en (**1**), and $Pb[S_2P(OPr^i)_2]$•bipy (**2**)

	(3)	(1)	(2)
Formula	$C_{18}H_{48}N_2O_8P_4Pb_2S_8$	$C_{10}H_{28}N_2O_4P_2PbS_4$	$C_{18}H_{28}N_2O_4P_2PbS_4$
M	1 215.4	637.7	733.8
Crystal class	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	9.997(2)	14.727(2)	10.933(2)
b/Å	14.875(2)	14.490(2)	13.257(2)
c/Å	15.000(2)	11.616(2)	13.705(2)
α/°	98.54(2)		103.58(1)
β/°	100.77(2)	110.72(2)	132.24(2)
γ/°	95.64(2)		91.50(2)
U/Å^3	2 148.7(6)	2 318(1)	1 382(1)
Z	2	4	2
D_m/g cm^{-3}		1.7[a]	1.84[b]
D_c/g cm^{-3}	1.88	1.83	1.76
F(000)	1 172	1 240	716
No. of independent reflections	1 723		4 317
R	0.0765	1 869	0.0853
Crystal size (mm)	0.3 × 0.3 × 0.3	0.0497	0.3 × 0.03 × 0.8
μ(Mo-K_α)/cm^{-1}	82.53	0.05 × 0.3 × 0.5	64.36
λ(Mo-K_α)/Å	0.7107	76.55	0.7107
Weighting scheme		0.7107	
A(0)		255.87	
A(1)		390.68	
A(2)		178.73	
A(3)		38.33	

[a] Flotation method in hexachlorobuta-1,3-diene–hexane. [b] Flotation method in hexachlorobuta-1,3-diene–bromoform.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results

Description of the Structures.—Crystals of $Pb[S_2P(OEt)_2]_2$•bipy (**2**) comprise discrete centrosymmetric binuclear molecules formed by the 'head-to-tail' dimerization of two monomer $\{Pb[S_2P(OEt)_2]_2$•bipy$\}$ units (Figure 1). The central feature of these dimer molecules is a rectangular four-membered Pb_2S_2 ring [S(1')–Pb(1)–S(1) 89.1(2), Pb(1')–S(1)–Pb(1) 90.9(2)°, Pb(1)–S(1) 3.118(7), Pb(1)–S(1') 3.212(6) Å]. Each lead atom is chelated by two dithiophosphato groups forming two coplanar PbS_2P rings. However, whilst one dithiophosphate chelates the lead atom almost symmetrically [Pb–S 2.929(7) and 2.948(7) Å], the other chelates in an anisobidentate fashion [Pb–S 3.000(6) and 3.118(7) Å] due to the participation of one sulphur atom, S(1), in bridging to the second lead atom of the dimer molecule. The co-ordination polyhedron of each lead atom, which approximates to a pentagonal bipyramid, is completed by the bridging sulphur atom and an essentially symmetrically bidentate bipyridine molecule [Pb–N 2.58(2) and 2.63(2) Å]. The distortion of the pentagonal bipyramid is such to preclude stereochemical activity of the non-bonding electron pair of the bivalent lead atom. Thus, the angle between the two atoms in axial positions [N(1) and S(1')] is 173.9(5)°, the sum of the angles subtended at lead by the equatorial atoms [N(2), S(1), S(2), S(3), and S(4) is 361.1°], and, except for the angles involving N(2), the axial–equatorial angles fall in the range 85.3(5)—96.9(2)°.

In contrast to the molecular structure of (**2**), both ethylenediamine complexes exhibit one-dimensional polymeric structures. That of $Pb[S_2P(OEt)_2]_2$•en (**1**) is illustrated

Table 3. Final fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for $\{Pb[S_2P(OEt)_2]_2\}_2\cdot en$ (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pb(1)	0.433 0(2)	0.119 1(1)	0.122 4(1)	O(6)	−0.312(4)	0.199(2)	0.864(3)
Pb(2)	0.005 2(2)	0.181 9(1)	0.862 0(1)	O(7)	0.177(5)	0.365(3)	0.652(3)
P(1)	0.568(2)	0.137(1)	0.359(1)	O(8)	0.040(4)	0.218(3)	0.585(3)
P(2)	0.245(2)	0.306 0(9)	0.104(1)	C(1)	0.610(8)	−0.031(6)	0.372(4)
P(3)	−0.345(1)	0.134 8(8)	0.934(1)	C(2)	0.692(7)	−0.064(5)	0.446(4)
P(4)	0.094(2)	0.289(1)	0.688(1)	C(3)	0.517(8)	0.299(6)	0.457(7)
S(1)	0.692(2)	0.157(1)	0.273(1)	C(4)	0.58(1)	0.360(4)	0.542(6)
S(2)	0.372(2)	0.108(1)	0.297(1)	C(5)	0.22(1)	0.366(7)	0.271(6)
S(3)	0.445(2)	0.321(1)	0.149(2)	C(6)	0.214(9)	0.438(5)	0.332(5)
S(4)	0.162(1)	0.177 7(8)	0.071 9(9)	C(7)	0.24(1)	0.435(3)	0.000(7)
S(5)	−0.538(1)	0.078 7(8)	0.905 7(9)	C(8)	0.12(2)	0.485(8)	−0.031(7)
S(6)	−0.206(1)	0.049 4(7)	0.937 3(9)	C(9)	−0.184(5)	0.249(4)	1.077(5)
S(7)	0.214(1)	0.224(1)	0.769(1)	C(10)	−0.204(8)	0.335(5)	1.135(5)
S(8)	−0.061(2)	0.330(1)	0.737(1)	C(11)	−0.392(7)	0.281(4)	0.854(5)
N(1)	0.093(5)	0.030(3)	0.841(4)	C(12)	−0.384(5)	0.306(5)	0.771(6)
N(2)	−0.117(3)	0.083(2)	0.716(3)	C(13)	0.23(1)	0.451(6)	0.718(5)
O(1)	0.610(4)	0.061(4)	0.420(3)	C(14)	0.25(1)	0.515(5)	0.647(6)
O(2)	0.591(5)	0.226(4)	0.443(3)	C(15)	−0.049(7)	0.226(8)	0.47(1)
O(3)	0.178(3)	0.360(2)	0.177(3)	C(16)	0.052(7)	0.268(8)	0.47(1)
O(4)	0.200(4)	0.353(2)	0.016(3)	C(17)	0.014(7)	−0.142(4)	0.777(5)
O(5)	−0.317(4)	0.205(2)	1.031(2)	C(18)	0.047(4)	0.007(3)	0.689(3)

Table 4. Final interatomic distances (Å) and angles (°) with e.s.d.s in parentheses for $\{Pb[S_2(OEt)_2]_2\}_2\cdot en$ (**3**)

Pb(1)–S(1)	3.05(2)	P(2)–O(3)	1.55(4)
Pb(1)–S(2)	2.82(1)	P(2)–O(4)	1.61(4)
Pb(1)–S(3)	2.96(1)	P(3)–O(5)	1.61(4)
Pb(1)–S(4)	2.93(1)	P(3)–O(6)	1.58(3)
Pb(1)–S(5)	3.21(1)	Pb(2)–S(7)	2.80(1)
Pb(1)–S(6)	3.11(1)	Pb(2)–S(8)	3.15(2)
Pb(1)–S(5′)	3.29(1)	Pb(2)–S(4′)	3.26(1)
S(1)–P(1)	1.98(2)	Pb(2)–S(6′)	3.22(1)
S(2)–P(1)	1.99(3)	Pb(2)–N(1)	2.50(3)
S(3)–P(2)	1.96(2)	Pb(2)–N(2)	2.48(4)
S(4)–P(2)	1.96(2)	S(7)–P(4)	1.97(2)
S(5)–P(3)	1.96(2)	S(8)–P(4)	1.95(2)
S(6)–P(3)	1.97(2)	P(4)–O(7)	1.55(4)
P(1)–O(1)	1.60(5)	P(4)–O(8)	1.69(4)
P(1)–O(2)	1.65(4)		
S(1)–Pb(1)–S(2)	68.5(4)	Pb(1)–S(3)–P(2)	89.1(7)
S(1)–Pb(1)–S(3)	84.7(6)	Pb(1)–S(1)–P(2)	90.0(6)
S(1)–Pb(1)–S(4)	142.0(4)	Pb(1)–S(5)–P(3)	93.2(6)
S(1)–Pb(1)–S(5)	80.8(4)	Pb(1)–S(6)–P(3)	91.4(6)
S(1)–Pb(1)–S(6)	131.1(4)	S(1)–P(1)–S(2)	113(1)
S(1)–Pb(1)–S(5′)	119.1(4)	S(1)–P(1)–O(1)	113(2)
S(2)–Pb(1)–S(3)	93.6(5)	S(1)–P(1)–O(2)	111(2)
S(2)–Pb(1)–S(4)	87.1(4)	O(1)–P(1)–O(2)	98(3)
S(2)–Pb(1)–S(5)	95.3(4)	S(2)–P(1)–O(1)	110(2)
S(2)–Pb(1)–S(6)	81.9(4)	S(2)–P(1)–O(2)	96(2)
S(2)–Pb(1)–S(5′)	165.3(4)	S(3)–P(2)–S(4)	113(1)
S(3)–Pb(1)–S(4)	67.6(4)	S(3)–P(2)–O(3)	110(2)
S(3)–Pb(1)–S(5)	158.8(4)	S(3)–P(2)–O(4)	113(2)
S(3)–Pb(1)–S(6)	136.9(4)	O(3)–P(2)–O(4)	102(2)
S(3)–Pb(1)–S(5′)	99.4(5)	S(4)–P(2)–O(3)	111(1)
S(4)–Pb(1)–S(5)	132.0(4)	S(4)–P(2)–O(4)	107(2)
S(4)–Pb(1)–S(6)	69.3(3)	S(5)–P(3)–S(6)	116.2(7)
S(4)–Pb(1)–S(5′)	91.7(3)	S(5)–P(3)–O(5)	109(1)
S(5)–Pb(1)–S(6)	63.7(3)	S(5)–P(3)–O(6)	113(2)
S(5)–Pb(1)–S(5′)	74.7(3)	O(5)–P(3)–O(6)	103(2)
S(6)–Pb(1)–S(5′)	84.0(3)	S(6)–P(3)–O(5)	110(1)
Pb(1)–S(1)–P(1)	86.0(9)	S(6)–P(3)–O(6)	105(1)
Pb(1)–S(2)–P(1)	92.3(7)		

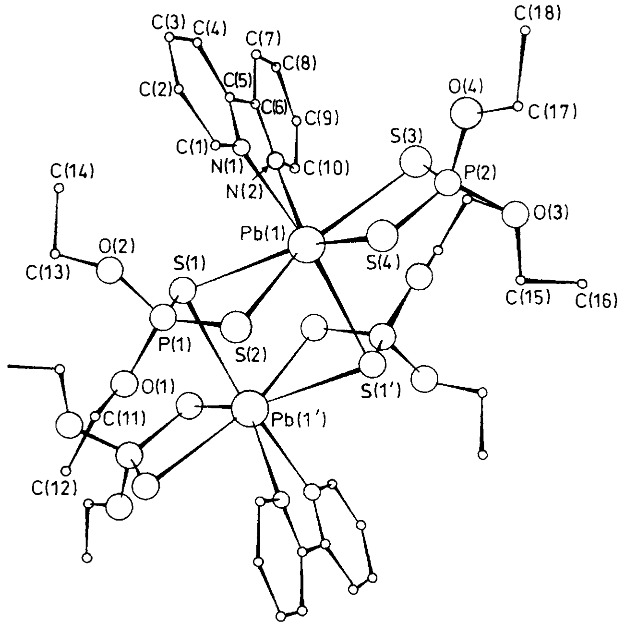

Figure 1. View of the dimeric molecules of $Pb[S_2P(OEt)_2]_2\cdot bipy$ (**2**), showing the atomic numbering

in Figure 2, and as in the structure of (**2**), adjacent $\{Pb\{S_2P(OEt)_2]_2\cdot en\}$ units are bridged nearly symmetrically [Pb–S 3.173(5) and 3.190(5) Å] by a sulphur atom. One dithiophosphato group chelates the lead atom whilst the other both chelates this atom, and additionally forms a sulphur bridge to an adjacent lead atom. Both the chelating and the chelating/bridging dithiophosphato groups, which are not coplanar, and the ethylenediamine ligand, chelate in an anisobidentate manner [Pb–S 2.967(5) and 3.177(5) Å (chelating ligand); 3.074(5) and 3.173(5) Å (chelating/bridging ligand); Pb–N 2.50(1) and 2.57(1) Å]. In spite of the similarity of the mode of bonding of the ligands to lead, as observed in the bipyridine complex (**2**), the resulting co-ordination polyhedron in the ethylenediamine complex (**1**) is quite different and is best described as a distorted square antiprism in which one co-ordination site is vacant. The four sites of the square base of the antiprism are occupied by the two sulphur atoms of the chelating dithiophosphato group and the two nitrogen atoms of the ethylenediamine ligand. Of the other four antiprismatic

Table 5. Final fractional atomic co-ordinates with e.s.d.s in parentheses for $Pb[S_2P(OEt)_2]_2 \cdot en$ (**1**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pb(1)	0.352 28(5)	0.238 10(4)	0.410 00(6)	O(4)	0.109(2)	0.465(1)	0.383(3)
S(1)	0.441 9(4)	0.275 3(3)	0.210 9(4)	C(1)	0.236(3)	0.049(2)	0.278(2)
S(2)	0.523 0(4)	0.113 9(4)	0.423 6(5)	C(2)	0.248(2)	0.028(2)	0.395(3)
S(3)	0.158 2(4)	0.276 8(4)	0.430 5(5)	C(3)	0.469(2)	−0.011(1)	0.162(2)
S(4)	0.244 0(4)	0.410 8(4)	0.260 3(5)	C(4)	0.386(2)	−0.059(1)	0.066(2)
P(1)	0.506 1(4)	0.155 8(3)	0.256 9(5)	C(5)	0.623(2)	0.197(3)	0.282(4)
P(2)	0.137 6(4)	0.380 3(4)	0.315 9(6)	C(6)	0.728(3)	0.248(2)	0.216(4)
N(1)	0.250(1)	0.143(1)	0.239(1)	C(7)	0.019(4)	0.362(4)	0.081(5)
N(2)	0.312(1)	0.082 2(9)	0.493(1)	C(8)	−0.074(3)	0.357(3)	0.008(4)
O(1)	0.442(1)	0.086 2(8)	0.155(1)	C(9)	0.104(3)	0.543(3)	0.380(5)
O(2)	0.603(1)	0.149(1)	0.230(2)	C(10)	0.068(4)	0.601(3)	0.439(5)
O(3)	0.040(1)	0.363(2)	0.204(2)				

Table 6. Final interatomic distances (Å) and angles (°) with e.s.d.s in parentheses for $Pb[S_2P(OEt)_2]_2 \cdot en$ (**1**)

Pb(1)–S(1)	3.173(5)	S(2)–P(1)	1.958(7)
Pb(1)–S(1′)	3.190(5)	S(3)–P(2)	1.957(7)
Pb(1)–S(2)	3.074(5)	S(4)–P(2)	1.945(8)
Pb(1)–S(3)	2.967(5)	P(1)–O(1)	1.59(1)
Pb(1)–S(4)	3.177(5)	P(1)–O(2)	1.57(2)
Pb(1)–N(1)	2.50(1)	P(2)–O(3)	1.58(2)
Pb(1)–N(2)	2.57(1)	P(2)–O(4)	1.59(2)
S(1)–P(1)	1.955(6)		
S(1)–Pb(1)–S(1′)	133.9(1)	Pb(1)–S(1)–Pb(1′)	132.2(2)
S(1)–Pb(1)–S(2)	63.8(1)	Pb(1)–S(1)–P(1)	86.1(2)
S(1)–Pb(1)–S(3)	132.2(1)	Pb(1′)–S(1)–P(1)	102.5(2)
S(1)–Pb(1)–S(4)	71.8(1)	Pb(1)–S(2)–P(1)	88.9(2)
S(1)–Pb(1)–N(1)	75.6(4)	Pb(1)–S(3)–P(2)	91.8(2)
S(1)–Pb(1)–N(2)	128.0(3)	Pb(1)–S(4)–P(2)	85.9(2)
S(1′)–Pb(1)–S(2)	85.1(1)		
S(1′)–Pb(1)–S(3)	90.1(1)	S(1)–P(1)–S(2)	115.2(3)
S(1′)–Pb(1)–S(4)	126.6(1)	S(3)–P(2)–S(4)	116.8(3)
S(1′)–Pb(1)–N(1)	138.9(4)	S(1)–P(1)–O(1)	104.9(5)
S(1′)–Pb(1)–N(2)	69.0(4)	S(2)–P(1)–O(1)	112.1(5)
S(2)–Pb(1)–S(3)	154.8(2)	O(1)–P(1)–O(2)	99(1)
S(2)–Pb(1)–S(4)	135.5(1)	S(1)–P(1)–O(2)	112.8(6)
S(2)–Pb(1)–N(1)	86.7(4)	S(2)–P(1)–O(2)	111.7(7)
S(2)–Pb(1)–N(2)	76.3(3)	S(3)–P(2)–O(3)	108.5(9)
S(3)–Pb(1)–S(4)	65.4(1)	S(4)–P(2)–O(3)	111.5(9)
S(3)–Pb(1)–N(1)	80.7(4)	O(3)–P(2)–O(4)	102(2)
S(3)–Pb(1)–N(2)	78.9(3)	S(3)–P(2)–O(4)	105.1(9)
S(4)–Pb(1)–N(1)	85.5(4)	S(4)–P(2)–O(4)	111.9(9)
S(4)–Pb(1)–N(2)	139.5(4)		

Primed atoms are related by the symmetry operation *x*, ½ − *y*, ½ + *z*.

sites, two are occupied by mutally *trans* bridging sulphur atoms and one other by the second sulphur of the chelating/bridging dithiophosphato group. The vacancy in the co-ordination polyhedron opposite this sulphur atom may be ascribed to stereochemical activity for the bivalent lead non-bonded electron pair.

The structure of the 2:1 ethylenediamine complex, $\{Pb[S_2P(OEt)_2]_2\}_2 \cdot en$ (**3**), is much more complex and comprises tetranuclear units containing two different types of lead atoms linked together to form chains. These complex chains extending along the crystal *a* axis are composed of dimeric $\{Pb[S_2P(OEt)_2]_3\}_2$ units doubly bridged by $Pb[S_2P(OEt)_2] \cdot en$ units. The tetranuclear repeating unit of the structure has a crystallographically imposed centre of inversion, and is illustrated in Figure 3. The central feature of the $\{Pb[S_2P(OEt)_2]_3\}_2$ dimer units is a central planar, lozenge-shaped four-membered Pb_2S_2 ring [Pb(1)–S(5) 3.21(1) and Pb(1)–S(5′) 3.29(1) Å, S(5)–Pb(1)–S(5′) 74.7(3) and Pb(1)–S(5)–Pb(1) 105.1(3)°]. The co-ordination polyhedron of the lead atoms in the dimer unit

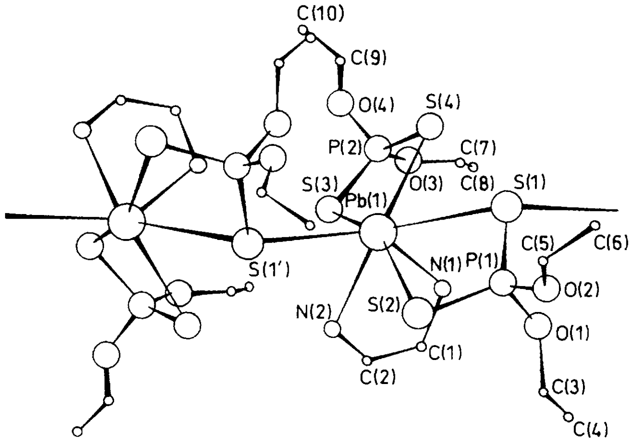

Figure 2. View of the linear chain structure of $Pb[S_2P(OEt)_2]_2 \cdot en$ (**1**), showing the atomic numbering

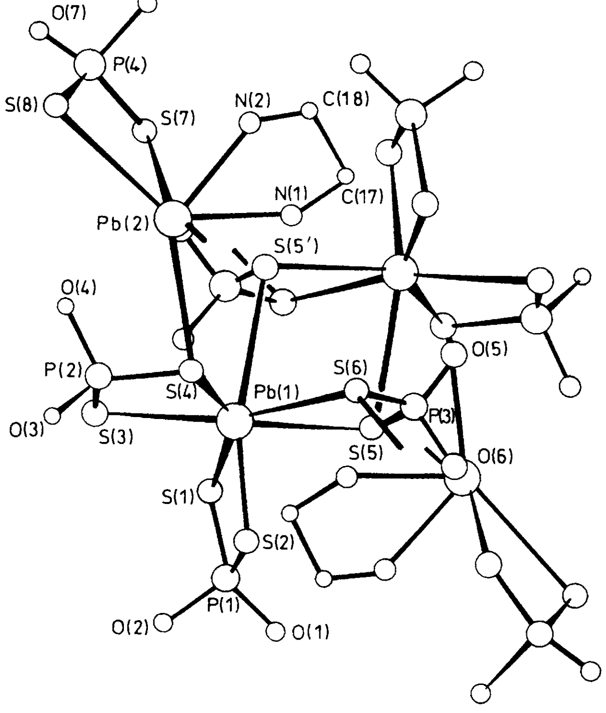

Figure 3. The polymeric structure of $\{Pb[S_2P(OEt)_2]_2\}_2 \cdot en$ (**3**) viewed along the direction of propagation of the chain, showing the atomic numbering. Ethyl groups have been omitted for clarity

Table 7. Final fractional atomic co-ordinates with e.s.d.s in parentheses for $Pb[S_2P(OEt)_2]_2$·bipy (**2**)

Atom	*X/a*	*Y/b*	*Z/c*
Pb(1)	0.131 0(1)	0.171 76(6)	0.071 94(8)
S(1)	−0.102 4(8)	0.059 6(5)	0.091 8(6)
S(2)	0.322 7(8)	0.102 8(5)	0.323 9(6)
S(3)	0.180(1)	0.292 1(6)	−0.059 6(8)
S(4)	0.493 9(9)	0.259 7(7)	0.242 2(7)
P(1)	0.114 5(8)	0.077 8(5)	0.294 7(6)
P(2)	0.428 0(9)	0.310 7(5)	0.090 9(8)
N(1)	0.146(2)	0.347(1)	0.214(2)
N(2)	−0.133(2)	0.255(2)	−0.065(2)
O(1)	0.089(2)	−0.025(1)	0.317(2)
O(2)	0.142(2)	0.178(1)	0.397(2)
O(3)	0.503(2)	0.260(1)	0.033(2)
O(4)	0.519(3)	0.435(2)	0.151(3)
C(1)	0.277(3)	0.384(2)	0.355(2)
C(2)	0.295(3)	0.480(2)	0.437(2)
C(3)	0.177(4)	0.540(2)	0.372(3)
C(4)	0.042(4)	0.503(2)	0.227(3)
C(5)	0.029(3)	0.404(2)	0.151(2)
C(6)	−0.116(3)	0.358(2)	−0.004(2)
C(7)	−0.226(4)	0.421(2)	−0.081(3)
C(8)	−0.362(4)	0.369(3)	−0.227(3)
C(9)	−0.380(3)	0.263(2)	−0.289(3)
C(10)	−0.262(4)	0.206(2)	−0.204(2)
C(11)	0.222(5)	−0.032(3)	0.458(3)
C(12)	0.174(5)	−0.131(3)	0.458(4)
C(13)	0.008(5)	0.181(3)	0.394(4)
C(14)	−0.054(5)	0.273(4)	0.356(4)
C(15)	0.451(5)	0.142(2)	−0.035(4)
C(16)	0.448(6)	0.119(3)	−0.146(4)
C(17)	0.679(6)	0.472(3)	0.212(6)
C(18)	0.725(5)	0.592(3)	0.253(4)

Table 8. Final interatomic distances (Å) and angles (°) with e.s.d.s in parentheses for $Pb[S_2P(OEt)_2]_2$·bipy (**2**)

Pb(1)–S(1)	3.118(7)	S(2)–P(1)	1.95(1)
Pb(1)–S(1′)	3.212(6)	S(3)–P(2)	1.97(1)
Pb(1)–S(2)	3.000(6)	S(4)–P(2)	1.99(1)
Pb(1)–S(3)	2.948(7)	P(1)–O(1)	1.60(2)
Pb(1)–S(4)	2.929(7)	P(1)–O(2)	1.61(2)
Pb(1)–N(1)	2.58(2)	P(2)–O(3)	1.55(2)
Pb(1)–N(2)	2.63(2)	P(2)–O(4)	1.60(2)
S(1)–P(1)	1.978(8)		
S(1)–Pb(1)–S(1′)	89.1(2)	S(1)–P(1)–O(2)	110.4(8)
S(1)–Pb(1)–S(2)	66.2(2)	S(2)–P(1)–O(2)	106.3(8)
S(1)–Pb(1)–S(3)	150.8(2)	S(3)–P(2)–O(3)	112.0(9)
S(1)–Pb(1)–S(4)	139.8(2)	S(4)–P(2)–O(3)	111.7(9)
S(1)–Pb(1)–N(1)	85.3(5)	O(3)–P(2)–O(4)	100(1)
S(1)–Pb(1)–N(2)	77.7(5)	S(3)–P(2)–O(4)	107(1)
S(1′)–Pb(1)–S(2)	87.3(2)	S(4)–P(2)–O(4)	112(1)
S(1′)–Pb(1)–S(3)	96.9(2)	P(1)–O(1)–C(11)	120(2)
S(1′)–Pb(1)–S(4)	95.8(2)	P(1)–O(2)–C(13)	119(2)
S(1′)–Pb(1)–N(1)	173.9(5)	P(2)–O(3)–C(15)	119(2)
S(1′)–Pb(1)–N(2)	118.3(4)	P(2)–O(4)–C(17)	124(3)
Pb(1)–S(1)–Pb(1′)	90.9(2)	S(2)–Pb(1)–S(3)	142.5(2)
Pb(1)–S(1)–P(1)	84.7(3)	S(2)–Pb(1)–S(4)	74.2(2)
Pb(1′)–S(1)–P(1)	99.6(3)	S(2)–Pb(1)–N(1)	88.3(4)
Pb(1)–S(2)–P(1)	88.4(3)	S(2)–Pb(1)–N(2)	135.5(5)
Pb(1)–S(3)–P(2)	88.8(3)	S(3)–Pb(1)–N(4)	68.4(2)
Pb(1)–S(4)–P(2)	89.0(3)	S(3)–Pb(1)–N(1)	90.1(5)
S(1)–P(1)–S(2)	116.5(4)	S(3)–Pb(1)–N(2)	74.6(5)
S(3)–P(2)–S(4)	113.2(5)	S(4)–Pb(1)–N(1)	87.0(5)
S(1)–P(1)–O(1)	106.2(7)	S(4)–Pb(1)–N(2)	131.7(5)
S(2)–P(1)–O(1)	112.8(8)	N(1)–Pb(1)–N(2)	62.8(5)
O(1)–P(1)–O(2)	104(9)		

Primed atoms are related by the symmetry operation $-x$, $-y$, $-z$.

comprises three chelating dithiophosphato groups and one bridging sulphur atom resulting in a distorted pentagonal bipyramidal geometry similar to that exhibited by the bipyridine complex (**2**). Thus, the angle subtended by the two sulphur atoms in the axial sites [S(2) and S(5′)] is 165.3(4)°, the sum of the angles subtended by the equatorial sulphur atoms [S(1), S(3), S(4), S(5), and S(6)] is 366.1°, and, except for the angles involving S(1), the angles between axial and equatorial sulphur atoms fall in the range 81.9(4)—99.4(5)°. As for (**2**) no apparent vacancy is seen in the co-ordination polyhedron indicating absence of stereochemical activity for the lead non-bonding electron pair. Each of the three dithiophosphato groups exhibits a different co-ordination mode. One simply chelates in a rather anisobidentate fashion [Pb(1)–S(2) 2.82(1) and Pb(1)–S(1) 3.05(2) Å]. The other two are not only involved in chelation but also participate in bridging to adjacent lead atoms. Of these, one forms a single long sulphur bridge [Pb(2)–S(4′) 3.26(1) Å] to a neighbouring $Pb[S_2P(OR)_2]$·en unit, whilst chelating symmetrically [Pb(1)–S(4) 2.93(1) and Pb(1)–S(3) 2.96(1) Å]. The other forms two such bridges, one to the other lead atom within the dimer unit and one to a second neighbouring $Pb[S_2P(OR)_2]$·en unit. In this case, all three lead–sulphur distances are long, with the two chelating distances [Pb(1)–S(6) 3.11(1) and Pb(1)–S(5) 3.21(1) Å] being only marginally shorter than the 'bridging' distance [Pb(2)–S(6′) 3.22(1) Å].

Co-ordination about lead in the $Pb[S_2P(OR)_2]$·en units is extremely unusual, and consists of four contacts to sulphur and two to nitrogen in a geometry which is best described as a distorted square-based pyramid, the apical site of which is occupied by a symmetrically chelating ethylenediamine [Pb–N 2.48(4) and 2.50(3) Å]. Of the four sulphur atoms in the highly distorted square base (sum of the S–Pb–S angles 376.7°), two are from an anisobidentate dithiophosphato group [Pb(2)–S(7) 2.80(1) and Pb(2)–S(8) 3.15(2) Å] and two are sulphur bridges [Pb(2)–S(6′) 3.22(1) and Pb(2)–S(4) 3.26(1) Å] from the $\{Pb[S_2P(OEt)_2]_3\}_2$ dimer units. Opposite the ethylenediamine is a large vacancy in the co-ordination polyhedron of this lead atom, for which the lead non-bonding electron pair does appear to be stereochemically active.

Pertinent selected structural data for *O,O′*-diorgano dithiophosphato complexes of lead in both the (II) and (IV) oxidation states are collected in Table 9. Only in one case, $PbPh_3[S_2P(OEt)_2]$, is the dithiophosphato ligand unidentate and the compound monomeric. In all other cases, the dithiophosphato group functions as either a chelating or a chelating/bridging ligand leading to co-ordination numbers between five and eight for lead. The Pb–S distances fall in the range 2.679(6)—3.232(10) Å except for that in $PbPh_3[S_2P(OEt)_2]$ which is only 2.554(6) Å. Bridging Pb···S distances are in general longer, but the range of values of bridging distances [2.985(12)—3.49(2) Å] does overlap significantly with the range for that of the directly bound atoms. A comparison of the bridging Pb···S distances in the two 'head-to-tail' dimeric molecules, $\{Pb[S_2P(OBu^i)_2]_2\}_2$ and $\{Pb[S_2P(OPr^i)_2]_2\}_2$·bipy, reveals quite unexpectedly that the latter compound, in which the lead has the higher co-ordination number and which presumably is more sterically crowded, has the lower bridging distance, *i.e.* is more tightly associated into dimeric molecules than is the former compound.

Infrared Spectra.—The i.r. spectra of the complexes exhibit

Table 9. Comparison of selected structural data for lead *O,O′*-dialkyl dithiophosphate compounds

Compound	Degree of association	Co-ordination number	Ligand bonding mode	Pb–S (chelating)[a]	Pb · · · S (bridging)[a]	P–S[a]	S–Pb–S[b]	Ref.
$Pb[S_2P(OEt)_2]_2$	Polymeric	8[c]	(*i*) chelating/bridging	2.759(4), 2.998(3)	3.49(2)	1.974(3), 2.008(4)	71.2(2)	*d*
			(*ii*) chelating/bridging	2.782(4), 3.035(4)	3.48(2)	1.967(4), 1.995(3)	70.4(2)	
$Pb[S_2P(OPr^i)_2]_2$	Polymeric	6	(*i*) chelating/bridging	2.761(7), 3.232(10)	2.985(12)	1.982(13), 2.000(14)	67.1(2)	*e*
			(*ii*) chelating/bridging	2.772(7), 3.175(9)	3.027(11)	1.944(12), 1.958(13)	66.6(2)	
$Pb[S_2P(OBu^i)_2]_2$	Dimeric	5	(*i*) chelating	2.762(5), 2.768(5)		1.958(7), 1.986(8)	73.1(2)	*d*
			(*ii*) chelating/bridging	2.755(5), 3.127(5)	3.444(5)	1.951(8), 1.994(6)	68.1(2)	
$Pb[S_2P(OPh)_2]_2$	Dimeric	6[f]	(*i*) chelating	2.732(6), 2.896(7)		1.958(7), 1.993(6)	71.9(2)	*d*
			(*ii*) chelating/bridging	2.753(5), 3.323(5)	3.215(6)	1.960(9), 1.984(6)	65.6(2)	
$Pb[S_2P(OPr^i)_2]_2$·bipy	Dimeric	7	(*i*) chelating	2.929(7), 2.948(7)		1.97(1), 1.99(1)	64.2(2)	*g*
			(*ii*) chelating/bridging	3.000(6), 3.118(7)	3.212(6)	1.95(1), 1.978(8)	66.2(2)	
$Pb[S_2P(OEt)_2]_2$·en	Polymeric	7	(*i*) chelating	2.967(5), 3.177(5)		1.945(8), 1.957(7)	65.4(1)	*g*
			(*ii*) chelating/bridging	3.074(5), 3.173(5)	3.190(5)	1.955(6), 1.958(7)	63.8(1)	
$\{Pb[S_2P(OEt)_2]_2\}_2$·en	Polymeric							*g*
	Lead (1)	7	(*i*) chelating	2.82(1), 3.05(2)		1.98(2), 1.99(3)	68.5(4)	
			(*ii*) chelating/bridging	2.93(1), 2.96(1)	3.26(1)	1.96(2), 1.96(2)	67.6(4)	
			(*iii*) chelating/doubly bridging	3.11(1), 3.21(1)	3.22(1), 3.29(1)	1.96(2), 1.97(2)	63.7(3)	
	Lead (2)	6	(*i*) chelating	2.80(1), 3.15(2)		1.95(2), 1.97(2)	67.1(4)	
$PbPh_3[S_2P(OEt)_2]$	Monomeric	4	unidentate	2.554(6)		1.923(7), 2.035(7)		*h*
$PbPh_2[S_2P(OCH_2Ph)_2]_2$	Dimeric	7	(*i*) chelating	2.723(6), 2.940(7)		1.93(1), 1.98(1)	69.9(2)	*h*
			(*ii*) chelating/bridging	2.679(6), 2.957(6)	3.69(1)	1.93(1), 2.01(1)	71.7(2)	

[a] In Å. [b] In °. [c] Two intermolecular Pb · · · O contacts at 3.01(1) and 3.03(1) Å. [d] Ref. 1. [e] S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 363. [f] Assuming that the phenyl ring occupies one co-ordination site. [g] This work. [h] M. G. Begley, C. Gaffney, P. G. Harrison, and A. T. Steel, *J. Organomet. Chem.*, 1985, **289**, 281.

Table 10. Selected i.r. data (cm^{-1})*

Compound	ν[(P)–O–C]			ν[P–O–(C)]		$\nu_{asym.}(PS_2)$		$\nu_{sym.}(PS_2)$	
$Pb[S_2P(OEt)_2]_2$	1 153s	1 098m		1 017s(br)	934s(br)	659s	652	572s	536s
$Pb[S_2P(OEt)_2]_2$·en	1 160m	1 102m		1 023s(br)	944s(br)	656s		576m	554m(br)
$Pb[S_2P(OEt)_2]_2$·bipy	1 156m(br)	1 100m		1 018s(br)	945s(br)	672s	656	574m	550m
$Pb[S_2P(OEt)_2]_2$·deen	1 162m	1 108m(br)		1 024s(br)	943s(br)	653s(br)		551s(br)	
$Pb[S_2P(OEt)_2]_2$·phen	1 158m	1 099m		1 022s	937s	672s		558m(br)	
$Pb[S_2P(OEt)_2]_2$·terpy	1 157m(br)	1 098w		1 019s(br)	946s	656s		553m	
$Pb[S_2P(OPr^i)_2]_2$	1 180m	1 140m	1 010m	956s(br)		658s	632	548s	
$Pb[S_2P(OPr^i)_2]_2$·en	1 177m	1 140m	1 103s	956s(br)		656s(br)	632	549s(br)	
$Pb[S_2P(OPr^i)_2]_2$·bipy	1 175m	1 138m	1 100s(br)	961s(br)		643s(br)		560s(br)	
$Pb[S_2P(OPr^i)_2]_2\cdot Et_2en$	1 178m	1 139m	1 104s(br)	987s(d)	957s	642s		552s	
$Pb[S_2P(OPr^i)_2]_2$·phen	1 175m	1 139m	1 104s(br)	979s(d)	949s	663s(br)		561m(d)	552m
$Pb[S_2P(OPr^i)_2]_2$·terpy	1 175m(br)	1 138m	1 106s	983s(d)	960s	654s	645(d)	549s	

* Recorded as KBr discs using a PE 683 spectrophotometer; m = medium, s = strong, br = broad, and d = less intense peak of doublet.

bands characteristic of the two three-atom P–O–C and PS_2 skeletal frameworks and are collected in Table 10. The positions of these bands are almost unchanged from those in the parent lead(II) bis[*O,O′*-diethyl and -di-isopropyl dithiophosphates]. The *O,O′*-diethyl dithiophosphato complexes exhibit two bands for the ν[(P)–O–C] mode at *ca.* 1 160 and 1 100 cm^{-1} and two bands for the ν[P–O–(C)] mode (1 020 and 942 cm^{-1}). For the *O,O′*-di-isopropyl dithiophosphato complexes, three bands are observed for the ν[(P)–O–C] mode at *ca.* 1 176, 1 139, and 1 104 cm^{-1}. However, only one band is observed for the ν[P–O–(C)] mode in the range 949—961 cm^{-1}, sometimes with a less intense shoulder on the higher wavenumber side. Both the $\nu_{asym.}(PS_2)$ and $\nu_{sym.}(PS_2)$ modes appear to be little affected by the nature of the organic group or complexation mode adopted. Either one or two bands are observed for each complex in the ranges 632—672 [$\nu_{asym.}(PS_2)$] and 536—576 cm^{-1} [$\nu_{sym.}(PS_2)$]. It would, appear, therefore, that even fairly gross changes in the mode of co-ordination of the *O,O′*-dialkyl dithiophosphato groups to lead have very little effect on the positions of the characteristic i.r. vibrations of these ligands.

Acknowledgements

We thank the S.E.R.C. and the Esso Petroleum Company Ltd. for support.

References

1 P. G. Harrison, A. Steel, G. Pelizzi, and C. Pelizzi, *Main Group Chem.*, 1988, **11**, 181.

2 J. R. Carruthers, CRYSTALS Crystallographic Package, Oxford University, 1975.

3 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

4 S. Motherwell, PLUTO Molecular and Crystal Structure Plotting Programme, Cambridge, 1974.

Received 14*th November* 1988; *Paper* 8/04518F