On the Crystal Structure of Dithiophosphorus Compounds. The Crystal Structure of $Pb[S_2P(C_2H_5)_2]_2$ at 293 K and $Cd_2[S_2P(C_2H_5)_2]_4$ at 173 K

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The crystal structures of $Pb[S_2P(C_2H_5)_2]_2$ (**1**) and $Cd_2[S_2P(C_2H_5)_2]_4$ (**2**) have been determined from single-crystal X-ray diffraction data at 293 and 173 K, respectively. **1**: triclinic, space group $P\bar{1}$, a = 10.720(11), b = 11.852(5), c = 20.995(5) Å, α = 95.02(3), β = 100.11(4), γ = 90.27(7)°, Z = 6. Final R = 0.053 for 3849 observed reflections with $I > 3\sigma_c(I)$. **2**: orthorhombic, space group *Pbca*, a = 11.959(4), b = 20.235(13), c = 13.747(5) Å, Z = 4, Final R = 0.040 for 2088 reflections with $I > 2\sigma_c(I)$. In **1** each Pb atom is surrounded by four S atoms, at 2.749(5)–3.196(7) Å, from two diethyldithiophosphinate ligands in the form of a pyramid with Pb in the apex and two further S atoms, at 3.091(6)–3.435(6) Å, on the the "free" side of the Pb atom. The latter Pb–S interactions result in a weak polymer formation. Two methyl groups are each disordered over two positions. The Pb coordination polyhedron may alternatively be described as a pentagonal bipyramid with one of the equatorial positions occupied by a lone pair. Compound **2** contains dimeric cadmium diethyldithiophosphinate complexes. The Cd atoms and the two bridging ligands form an eight-membered ring with a twisted chair conformation. Each Cd atom is also chelated to another ligand which is disordered, with one methyl group statistically distributed over two positions. The structural results for **1** and **2** are compared to those for other *p*-metal and transition metal complexes with dithiophosphorus ligands. Changes in the molecular packing and coordination geometry are often brought about by changing the substituent on the phosphorus atom.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Dialkyldithiophosphoric acids and their organic esters have for many years been used as, e.g., pesticides, antioxidants and oil additives. Substituted dithiophosphate, dithiophosphonate and dithiophosphinate ligands ($R_2PS_2^-$, where R is OC_xH_y or C_xH_y) also form complexes with a variety of metals in which they exhibit a great diversity of coordination patterns. Several reviews of the crystal structures and properties have been published in the past 20 years,[1–6] the most recent in 1989.[6] The negative charge is usually delocalized over the PS_2 unit, but structures with the charge localized on one sulfur atom are also known. The ligands can basically be divided into monodentate, bidentate and bridging ligands, but structural details often show more complex differentiation. By variation of the R group in $R_2PS_2^-$ structural variation is often observed. This can be illustrated by the two Zn complexes $Zn(S_2PR_2)_2$, which form dimers[7] if R = OC_2H_5 and infinite chains[8] if R = $OCH(CH_3)_2$. In order to document structural changes brought about by variation of R we report here the crystal structure of bis(diethyldithiophosphinato)lead(II), $Pb[S_2P(C_2H_5)_2]_2$, (subsequently denoted **1**) at room temperature and that of tetrakis(diethyldithiophosphinato)dicadmium(II), $Cd_2[S_2P(C_2H_5)_2]_4$, (**2**) at 173 K. The crystal structures of the lead complexes with R = $OCH(CH_3)_2$[9] and OC_2H_5[10] have been published previously. In the first structure the Pb coordination is described as a pentagonal bipyramid with one equatorial position occupied by a lone pair, while a PbS_4 pyramid is found in the second structure. Two Cd compounds with R = $OCH(CH_3)_2$[8] and C_2H_5[11] have previously been determined at room temperature. Both form dimers in the solid state. Since disorder obviously affected the reported coordination geometry around Cd in both compounds, we decided to redetermine the crystal structure of the ethyl-substituted compound at 173 K. The structural results for **1** and **2** will also be compared to those from a number of transition and *p*-metal complexes with substituted dithiophosphorus ligands.

Experimental

Compounds **1** and **2** were prepared as described by Kuchen *et al.*[12] Single-crystals of **1** were grown from 2-propanol by

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Table 1. Crystal data and parameters describing the intensity data collection and least-squares refinement.

Compound	$Pb[S_2P(C_2H_5)_2]_2$ (**1**)	$Cd_2[S_2P(C_2H_5)_2]_4$ (**2**)
T/K	293	173
M_r	513.6	837.7
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a/Å	10.720(11)	11.959(4)
b/Å	11.852(5)	20.235(13)
c/Å	20.995(5)	13.747(5)
α/°	95.02(3)	90
β/°	100.11(4)	90
γ/°	90.27(7)	90
V/Å^3	2615(3)	3327(1)
Z	6	4
D_x/g cm^{-3}	1.957(1)	1.673(1)
F(000)	1464	1680
μ/mm^{-1}	10.37	1.95
Crystal size	0.20×0.06×0.06 mm^3	radius 0.20 mm
Grid in absorption correction	10×10×10	sphere
Transmission factor	0.29–0.48	0.56
hkl range	0→12, −14→14, −24→24	−14→0, −24→0, −16→0
Standard reflections	331, 241, 207	$\bar{4}\,\bar{8}\,3$, $3\,\bar{7}\,\bar{4}$, $2\,\bar{6}\,\bar{5}$
Maximum variation(%)	12	3
No. of reflections measured	9949	3525
No. of unique reflections	8900	3525
No. of observed unique reflections	3849 [$I>3\sigma_c(I)$]	2088 [$I>2\sigma_c(I)$]
R_{int}	0.031	–
R, *wR*	0.053, 0.062	0.040, 0.053
S	1.40	1.31
No. of parameters	295	146
$(\Delta/\sigma)_{max}$	0.90	0.27
$\Delta\varrho_{max}/\Delta\varrho_{min}$/e Å^{-3}	1.95/−1.40	0.73/−0.51

slow evaporation, yielding colourless elongated triangular prisms. Single crystals of **2** were obtained by slow evaporation from a dioxane solution, yielding colourless crystals with an approximately spherical habit. Crystal data and parameters describing the data collection and least-squares refinements are given in Table 1. The intensity measurements were made on an Enraf–Nonius CAD-4 diffractometer at 293 K for **1** and 173 K for **2**; the cooling device used is described in Ref. 6. Graphite-monochromated Mo *K*α radiation was used (λ = 0.710 69 Å). Unit-cell dimensions were determined from a least-squares fit of the setting angles of 43 (**1**) and 25 (**2**) reflections in the range $7.5 < \theta < 20°$ (**1**) and $10 < \theta < 15°$ (**2**). Intensity data were collected for both structures in the range $6 < 2\theta < 50°$ with the ω/2θ scan technique, $\Delta\omega = a + 0.5° \tan\theta$ ($a = 0.7°$ for **1** and 0.8° for **2**). Three standard reflections were recorded regularly for each structure, with no significant variation for **2** but a 12 % decrease in intensity for **1**, for which a correction was made. The data were also corrected for Lorentz, polarization and absorption effects, the latter by numerical integration.

Determination and refinement of the structures

Both structures were solved by Patterson methods and from subsequent Δϱ maps. Refinements were carried out by the full-matrix least-squares method minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma_c^2(F_o) + (a\,F_o)^2]^{-1}$ (with σ_c taken from counting statistics). The parameter *a* (0.03 for **1** and 0.02 for **2**) was adjusted to give constant $<w(\Delta F)^2>$ in different $|F_o|$ and sin θ intervals. No extinction effects were detected in **1** or **2**. The data and final model were compared by probability-plotting[13] of ordered values of $\delta R_i = \Delta F_i/\delta(|F_o|_i)$ versus those expected for ordered normal deviates, $\sigma(|F_o|_i) = w^{-1/2}$. The results were slopes of 1.330(1) and 1.148(4), intercepts of 0.0998(2) and 0.103(4), and correlation coefficients of 0.9982 and 0.9866 for **1** and **2**, respectively.

Two of the ethyl groups in **1** exhibit orientational disorder of the terminal methyl group. Both groups were refined in two alternative positions with occupancy factors of 0.5. Owing to the high atomic displacement parameters for the carbon atoms, no attempt was made to locate the hydrogen atoms. Isotropic displacement parameters were used for the carbon atoms and anisotropic ones for all other atoms. Final atomic parameters for **1** are given in Table 2, with bond lengths and angles in Table 3.

The Δϱ maps for **2** indicated disorder in one of the ligands in this compound also. Two models of the disorder were tested. In the first account was taken of most of the disorder by the displacement parameters, and only one CH_3 group was distributed over two positions. In the second model, previously used by Wunderlich[11] for the room-

Table 2. Positional and displacement parameters for compound **1**.[a]

Atom	x	y	z	U_{eq}/Å^2
Pb1	0.29479(8)	0.20081(7)	0.20949(4)	0.0762(3)
Pb2	0.80928(8)	0.40867(7)	0.20302(4)	0.0738(3)
Pb3	1.04286(8)	0.49888(7)	0.40551(4)	0.0734(3)
P1	0.5042(5)	0.2180(5)	0.0980(3)	0.085(2)
P2	0.3359(7)	−0.0594(6)	0.2643(4)	0.115(3)
P3	0.8331(6)	0.6919(5)	0.2523(3)	0.088(3)
P4	0.9928(7)	0.3314(6)	0.0819(3)	0.102(3)
P5	1.3363(5)	0.4019(6)	0.3989(3)	0.090(3)
P6	0.8736(5)	0.2520(5)	0.4053(2)	0.076(2)
S1	0.3401(5)	0.1259(5)	0.0882(2)	0.083(2)
S2	0.5264(7)	0.3332(7)	0.1702(4)	0.144(4)
S3	0.1705(6)	0.0018(6)	0.2203(4)	0.118(3)
S4	0.4781(6)	0.0542(7)	0.2787(3)	0.121(3)
S5	0.6753(6)	0.6087(5)	0.2082(3)	0.096(3)
S6	0.9853(5)	0.5925(5)	0.2652(3)	0.089(2)
S7	0.8444(6)	0.4365(5)	0.0772(3)	0.095(3)
S8	1.0114(5)	0.2416(5)	0.1592(3)	0.086(2)
S9	1.1825(5)	0.3635(5)	0.3299(2)	0.087(2)
S10	1.3008(6)	0.5143(6)	0.4692(3)	0.119(3)
S11	0.7940(5)	0.3780(5)	0.3547(3)	0.092(2)
S12	1.0131(5)	0.3093(5)	0.4787(2)	0.086(2)
C1	0.518(4)	0.266(3)	0.018(2)	0.192(14)
C2	0.422(3)	0.346(3)	−0.007(2)	0.167(12)
C3	0.646(3)	0.117(3)	0.122(1)	0.137(10)
C4	0.642(3)	0.018(3)	0.083(2)	0.169(12)
C5	0.370(3)	−0.191(3)	0.224(2)	0.183(14)
C6	0.385(3)	−0.186(3)	0.156(2)	0.178(13)
C7	0.324(4)	−0.095(3)	0.351(2)	0.166(12)
C8A	0.233(8)	−0.170(6)	0.344(4)	0.191(29)
C8B	0.433(12)	−0.174(10)	0.389(6)	0.332(59)
C9	0.860(2)	0.819(2)	0.206(1)	0.116(8)
C10	0.899(3)	0.777(2)	0.144(1)	0.133(9)
C11	0.823(3)	0.769(3)	0.331(2)	0.143(11)
C12A	0.712(8)	0.818(7)	0.334(4)	0.194(29)
C12B	0.777(6)	0.714(6)	0.363(3)	0.150(22)
C13	0.999(4)	0.252(3)	0.005(2)	0.188(14)
C14	0.894(3)	0.176(3)	−0.005(2)	0.175(13)
C15	1.143(3)	0.412(3)	0.078(2)	0.149(11)
C16	1.177(3)	0.492(3)	0.129(2)	0.159(11)
C17	1.470(3)	0.443(3)	0.364(1)	0.147(10)
C18	1.439(4)	0.541(3)	0.328(2)	0.181(13)
C19	1.416(5)	0.273(4)	0.436(2)	0.227(21)
C20	1.349(4)	0.219(3)	0.458(2)	0.194(16)
C21	0.746(2)	0.184(2)	0.437(1)	0.104(7)
C22	0.797(3)	0.075(3)	0.474(2)	0.164(12)
C23	0.943(2)	0.146(2)	0.355(1)	0.095(7)
C24	0.843(2)	0.108(2)	0.293(1)	0.118(8)

[a]The displacement parameters are isotropic for carbon atoms; e.s.d.s are given in parenthesis. For C8 and C12 the occupancy of the A and B positions is 1/2. $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij}\, a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

temperature structure of $Cd_2[S_2P(C_2H_5)_2]_4$, both ethyl groups and one S atom were distributed over two positions. Since the first model resulted in a more regular ligand geometry than the second, it was adopted for the final cycles of refinement. The hydrogen atoms on the ligand without disorder could be located in a $\Delta\varrho$ map and included in the refinement with fixed positional and isotropic dis-

Table 3. Selected bond lengths (in Å) and angles (in °) in **1** with e.s.d.s in parenthesis; symmetry code: (i) $x-1, y, z$; (ii) $2-x, 1-y, 1-z$.

Pb1–S1	2.749(5)	P1–C3	1.96(3)
Pb1–S2	3.196(8)	P2–S3	2.020(10)
Pb1–S3	2.749(7)	P2–S4	1.994(11)
Pb1–S4	2.909(8)	P2–C5	1.77(4)
Pb1–S8^i	3.091(6)	P2–C7	1.93(3)
Pb1–S9^i	3.435(6)	P3–S5	1.991(9)
Pb2–S5	2.782(6)	P3–S6	2.010(8)
Pb2–S6	2.934(6)	P3–C9	1.91(3)
Pb2–S7	2.781(6)	P3–C11	1.84(3)
Pb2–S8	3.144(6)	P4–S7	2.018(10)
Pb2–S2	3.100(8)	P4–S8	1.999(8)
Pb2–S11	3.269(6)	P4–C13	1.81(4)
Pb3–S9	2.783(6)	P4–C15	1.89(3)
Pb3–S10	2.850(7)	P5–S9	2.016(8)
Pb3–S11	3.000(6)	P5–S10	1.989(9)
Pb3–S12	2.877(6)	P5–C17	1.80(3)
Pb3–S6	3.198(6)	P5–C19	1.91(5)
Pb3–S12^{ii}	3.316(6)	P6–S11	2.014(8)
P1–S1	2.036(8)	P6–S12	2.018(8)
P1–S2	1.931(10)	P6–C21	1.84(2)
P1–C1	1.85(4)	P6–C23	1.81(2)
S1–Pb1–S9^i	160.1(2)	S5–Pb2–S6	71.5(2)
S2–Pb1–S4	88.2(2)	S6–Pb2–S8	97.6(2)
S2–Pb1–S8^i	125.2(2)	S12–Pb3–S6	145.2(1)
S3–Pb1–S4	72.4(2)	S9–Pb3–S10	72.6(2)
S3–Pb1–S8^i	74.4(2)	S9–Pb3–S11	95.7(2)
S7–Pb2–S11	175.1(2)	S10–Pb3–S12^{ii}	86.1(2)
S2–Pb2–S5	75.0(2)	S11–Pb3–S12^{ii}	105.6(2)
S2–Pb2–S8	118.2(2)	S7–P4–S8	112.5(4)
S1–P1–S2	113.4(4)	C13–P4–C15	91.1(18)
C1–P1–C3	107.4(15)	S9–P5–S10	112.7(4)
S3–P2–S4	112.9(5)	C17–P5–C19	95.0(18)
C5–P2–C7	104.2(16)	S11–P6–S12	112.2(4)
S5–P3–S6	113.2(4)	C21–P6–C23	108.5(1)
C9–P3–C11	98.1(13)		

Table 4. Positional and equivalent isotropic displacement parameters for compound **2**, with e.s.d.s in parenthesis.[a]

Atom	x	y	z	U_{eq}/Å^2
Cd	0.01353(4)	0.09611(3)	0.04279(4)	0.0374(2)
S1	0.1720(2)	0.10278(10)	0.1658(1)	0.0468(6)
S2	−0.0349(2)	0.20870(11)	0.1322(2)	0.0673(9)
S3	0.0240(1)	0.11672(9)	−0.1405(1)	0.0391(6)
S4	−0.1539(1)	0.01857(8)	0.0471(1)	0.0346(5)
P1	−0.1341(1)	−0.04212(9)	0.1634(1)	0.0317(5)
P2	0.1034(2)	0.19003(10)	0.2079(1)	0.0473(7)
C1	−0.0899(7)	0.0040(4)	0.2686(5)	0.048(3)
C2	−0.0945(8)	−0.0330(5)	0.3647(6)	0.066(4)
C3	−0.2715(6)	−0.0765(4)	0.1905(6)	0.045(3)
C4	−0.3162(7)	−0.1197(4)	0.1092(7)	0.060(3)
C5	0.2051(8)	0.2570(4)	0.1932(8)	0.069(4)
C6	0.2438(10)	0.2664(6)	0.0884(9)	0.088(5)
C7	0.0833(18)	0.1913(7)	0.3417(8)	0.144(8)
C8A	0.0812(34)	0.1395(17)	0.3918(18)	0.109(15)
C8B	0.0227(22)	0.1440(14)	0.3900(24)	0.077(10)

[a]C8A and B both have the occupancy 1/2.

$U_{eq} = \frac{1}{3}\sum_i U_{ii}$.

Table 5. Selected bond lengths (in Å), bond angles (in °) and torsion angles (in °) in **2** with e.s.d.s in parenthesis; symmetry code (i): $-x, -y, -z$.

Cd–S1	2.543(2)	P2–S2	1.991(3)
Cd–S2	2.653(3)	P2–C5	1.831(9)
Cd–S3	2.557(2)	P2–C7	1.854(11)
Cd–S4	2.544(2)	C1–C2	1.52(1)
P1–S3^{i}	2.028(3)	C3–C4	1.51(1)
P1–S4	2.030(3)	C5–C6	1.54(2)
P1–C1	1.800(8)	C7–C8A	1.25(3)
P1–C3	1.823(7)	C7–C8B	1.37(3)
P2–S1	2.031(3)	C8A–C8B	0.71(5)
S1–Cd–S2	79.01(7)	C2–C1–p1	115.6(6)
S3^{i}–Cd–S4	99.32(6)	C4–C3–P1	112.8(6)
S3^{i}–P1–S4	113.8(1)	C6–C5–P2	113.4(7)
C1–P1–C3	107.3(4)	C8A–C7–P2	122.5(16)
S1–P2–S2	110.5(1)	C8B–C7–P2	122.7(16)
C5–P2–C7	100.7(6)	C8A–C7–C8B	31(2)
S3–Cd–S4–P1	150.64(9)	S4–P1–S3^{i}–Cd^{i}	−11.48(11)
Cd–S4–P1–S3^{i}	−78.34(12)	P1–S3^{i}–Cd^{i}–S4^{i}	92.63(9)

placement parameters. Final atomic parameters for **2** are shown in Table 4, with bond distances and angles in Table 5.

Atomic scattering factors and anomalous dispersion corrections were taken from Ref. 14. The calculations were carried out on VAX 11/780 and Microvax 3100 computers using the crystallographic program system described by Lundgren.[15] Lists of structure factors, anisotropic displacement parameters and hydrogen-atom parameters may be obtained from one of the authors (G.S.) on request.

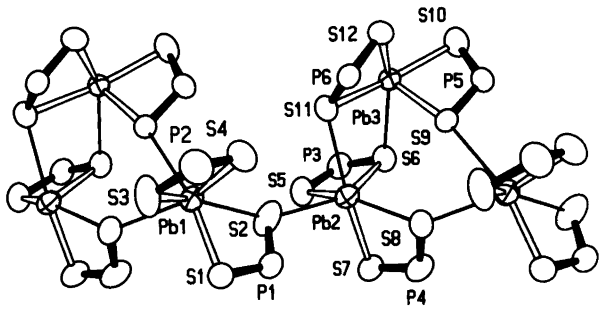

Fig. 1. The chain of $Pb[S_2P(C_2H_5)_2]_2$ complexes in compound **1** with the atom numbering scheme. Pb–S distances longer than 3.0 Å are indicated by thin lines. Carbon atoms are omitted for clairty. The thermal ellipsoids are scaled to include 50 % probability.

Description of the structures

$Pb[S_2P(C_2H_5)_2]_2$ (**1**). The asymetric unit comprises three monomeric lead complexes each involved in weak interactions with the others. This results in chain formation as shown in Fig. 1. Each lead atom is coordinated by two bidentate diethyldithiophosphinate ligands in an arrangement which may be described as a PbS_4 pyramid, with the four S atoms in the basal plane and the Pb atom in the apex, as illustrated in Fig. 2. This part of the irregular coordination polyhedron has Pb–S distances in the range 2.749(5)–3.196(7) Å, which agree well with distances found in other Pb dithiophosphorus complexes.[9,10] The length of a Pb–S covalent single bond is about 2.58 Å, while the ionic bond length is about 3.04 Å.[16] The orientation of the diethyldithiophosphinate ligands is similar to the arrangement in the diethyldithiophosphate analogue,[10] while the diisopropyl complex exhibits nearly planar $Pb(S_2PR_2)_2$ groups.[9] Each coordination polyhedron about Pb in **1** is completed by two S atoms on the "free" side of the Pb atom in the PbS_4 pyramid, at distances between 3.091(6) and 3.435(6) Å. These S atoms are provided by other PbS_4 units. The shorter distances clearly indicate ionic bonds connecting the $Pb(S_2PR_2)_2$ molecules in a polymeric chain. The crystal packing in the unit cell is shown in Fig. 3.

The Pb environment may also be described as a pentagonal bipyramid with one empty position in the equatorial plane (composed by S2, S4, S3 and S8 in Fig. 2, with similar arrangements about the other Pb atoms). The seventh ligand position might be occupied by the lone pair, as in the diisopropyl analogue. According to the VSEPR theory[17] the Pb–S bonds closest to the lone pair should be elongated and the S–Pb–S angle enlarged. The S–Pb–S angle on the opposite side should be diminished. An alternative approach to the stereochemistry of valence bonds has been argued by Andersson.[18] The volume of the lone pair is of

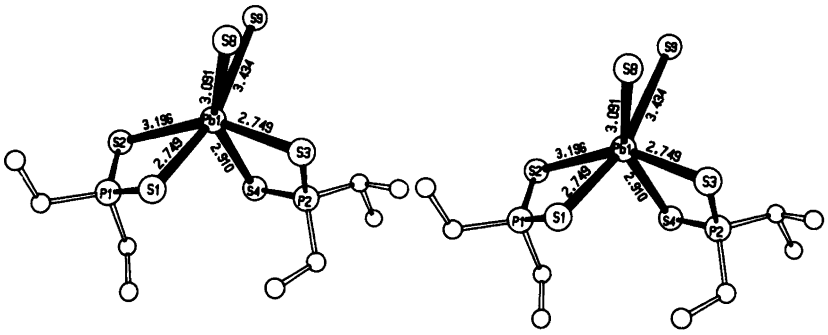

Fig. 2. The environment around Pb1 in **1** (similar to those around Pb2 and Pb3). Atoms are drawn on an arbitrary scale in Figs. 2 and 3.

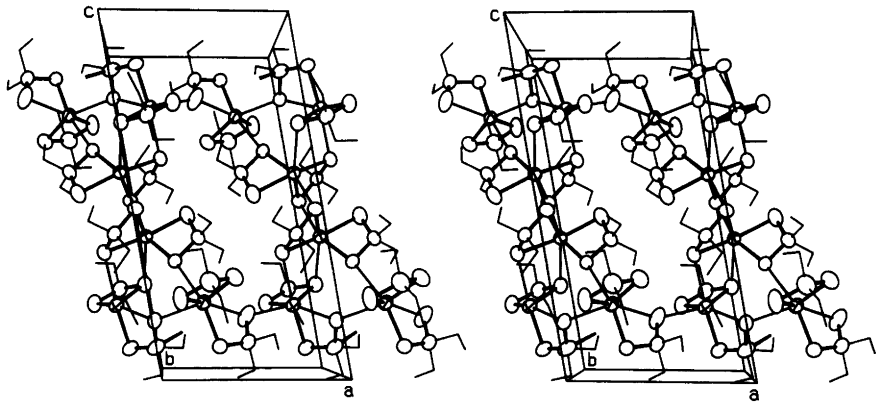

Fig. 3. Unit-cell content (crystal packing) of $Pb[S_2P(C_2H_5)_2]_2$ (**1**).

the same order of magnitude as that of O^{2-} and F^-, with the coordination geometry being governed by the difference in nucleus–lone pair and nucleus–bonding pair attraction forcing the nucleus off-centre in an otherwise regular polyhedron. Both approaches locate the Pb1 lone pair in the S2–S4–S3–S8 equatorial plane between S2 and S8 and the Pb2 and Pb3 lone pairs in corresponding positions.

The P–S distances are between 1.989(9) and 2.036(8) Å, excluding the P1–S2 bond with a length of 1.931(10) Å. This value is less reliable than the rest because of the large displacement parameters of S2. Thus the unequal Pb–S bond lengths are not reflected in unequal P–S bond lengths in the ligands. The negative charge is distributed equally over the two S atoms in each ligand. The average S–P–S angle is 112.8(4)°, which is slightly larger than normal,[6] as some of the S atoms interact with two Pb atoms. A detailed discussion of the ligand geometry is not particularly meaningful, since the displacement parameters are quite large. The ligand conformations may be described by the orientation of the ethyl groups, i.e. by the torsion angle C–P–C–C. Using the nomenclature of Klyne and Prelog,[18] the following conformations of the $P(C_2H_5)_2$ groups are observed: (*−ap*,*−sc*), (*−ap*,*+sc*), (*+ap*,*+sc*), (*+ap*,*+ap*), (*+sc*,*+ac*) and (*+ap*,*−ap*).*

$Cd_2[S_2P(C_2H_5)_2]_4$ (**2**). The crystal structure of this compound has been previously determined at room temperature by Wunderlich.[11] The model employed by him included split positions for five atoms, which resulted in an irregular ligand geometry. In the present model, based on 173 K data, only one atom has been treated as disordered over two positions, resulting in a much improved geometry. Fig. 4 shows that a dimeric complex is formed across a crystallographic centre of symmetry by two ligands forming Cd–S–P–S–Cd bridges. Each Cd atom is further bonded to a bidentate ligand, making the environment approximately tetrahedral. The conformation of the eight-membered ring formed by the dimerisation is a twisted chair (see below).

* *sp*: 0–30, *sc*: 30–90, *ac*: 90–150, *ap*: 150–180°; the minus signs indicate negative torsion angles.

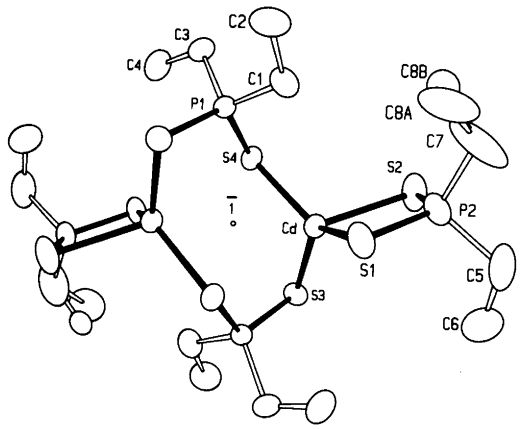

Fig. 4. The dimeric complex $Cd_2[S_2P(C_2H_5)_2]_4$ in compound **2** with the atom numbering scheme. The thermal ellipsoids are scaled to include 50 % probability.

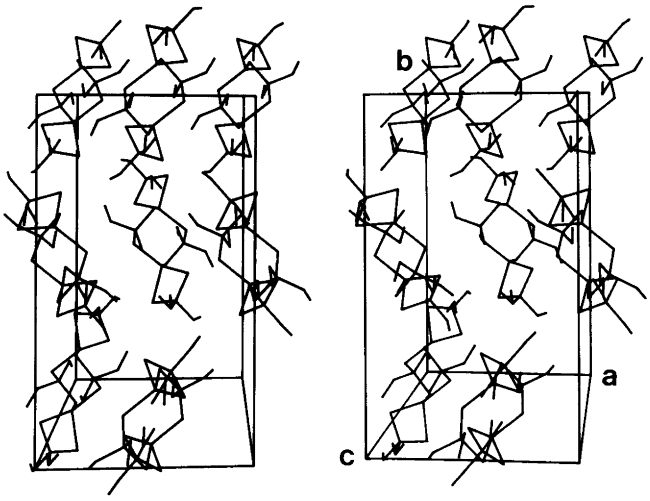

Fig. 5. Unit-cell content (crystal packing) of $Cd_2[S_2P(C_2H_5)_2]_4$ (**2**).

The chelating ligand is disordered, which can be seen from the enlarged displacement parametres, but the disorder cannot be resolved in separate positions. The conformation of the ethyl groups are $(+/-ap,-ap)$ for the chelating ligand and $(+sc,-ap)$ for the bridging ligand. The S–P–S angle is slightly larger in the bridging than in the chelating ligand, 113.8(1) and 110.5(1)°, respectively. The P–S bonds are almost identical, with an average length of 2.02(2) Å. The crystal packing is shown in Fig. 5.

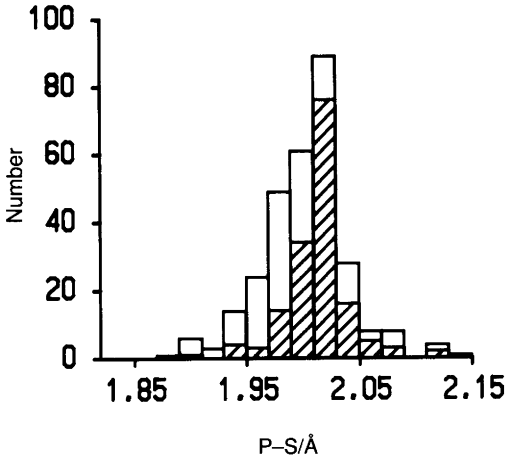

Fig. 6. A histogram of the variation in the P–S bond length in 68 dithiophosphorus compounds.[6] Shaded areas relate to dithiophosphinates and unshaded to dithiophosphates. References to and geometrical data for all compounds on which Figs. 6–9 are based are available on request from one of the authors (G.S.).

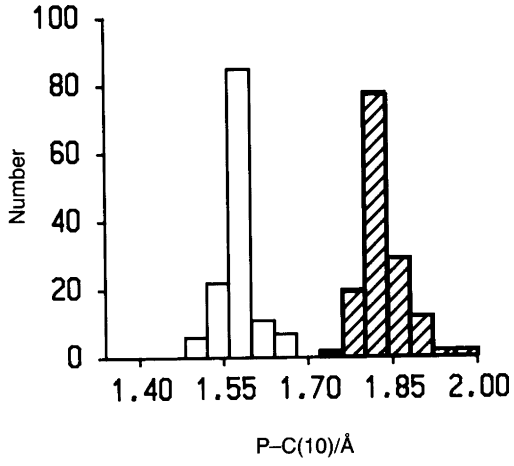

Fig. 7. Histograms of the P–C bond length variation in dithiophosphinate (shaded area) and P–O bond length variation in dithiophosphate compounds (unshaded area), cf. the legend to Fig. 6.

Discussion

The vast amount of structural data presented in the review articles,[1-6] makes it obvious that coordination compounds with dithiophosphorus ligands constitute a fruitful area for structure research. The following discussion is mainly connected with Ref. 6. According to Pauling's[16] scheme for summing covalent radii, the bond lengths of a single and double P–S bond should be 2.14 and 1.94 Å, respectively. Fig. 6 shows the variation in the P–S bond length for 68 dithiophosphate, dithiophosphonate and dithiophosphinate compounds. The maximum and minimum bond lengths agree rather well with the single and double bond lengths, respectively, but most of the bonds are intermediate, indicating that the negative charge is delocalized over the PS_2 group. The two P–S bond lengths are equal in the transition-metal complexes, while several examples are known among the *p*-metal compounds with unequal bond lengths. $Ni[S_2P(OCH(CH_3)_2)(C_2H_5)]_2$ is the only known transition metal complex with unequal bonds, 1.901(1) and 2.031(1) Å,[20] while the Sb and Sn complexes are examples from the *p*-elements.[21,22]

The variation in the P–C and P–O bond lengths for solid dithiphosphinate and dithiophosphate complexes are shown in Fig. 7. The large spread is probably mostly dependent on the varying precision and accuracy of the determinations. The variation in the S–P–S angle is shown in Fig. 8. The largest angles are found in the salts, e.g. $NaS_2P(C_2H_5)_2 \cdot 2H_2O$ [115.77(7)°],[23] and where the ligand acts as a bridge, forming an eight-membered ring (as in **2**). The angles in **1** are also larger than the tetrahedral angle, since several S atoms interact with two Pb atoms. The S–P–S angle is generally greater than the C/O–P–O/C angle because of the difference in size between the S atom and the C (dithiophosphinates) or O (dithiophosphates) atom. In

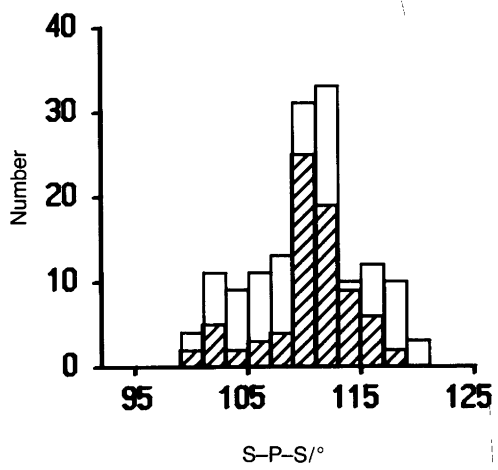

Fig. 8. A histogram showing the variation in the S–P–S angle in the 68 compounds of Fig. 6. Shaded areas relate to dithiophosphinate and unshaded to dithiophosphate compounds.

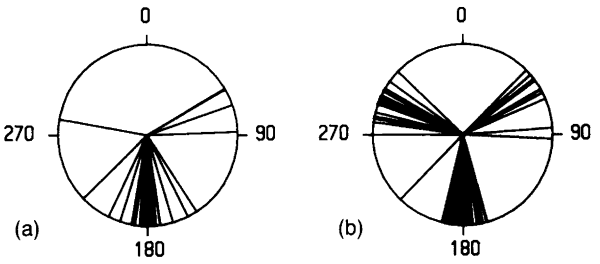

Fig. 9. Diagrams of the ester group in 13 dimethyl and diethyldithiophosphates (a) and of the ethyl group in 13 diethyldithiophosphinates (b), cf. the legend to Fig. 6.

Fig. 9 the ester group conformation in 13 solid dimethyl and diethyldithiophosphates is compared with the conformation of the ethyl group in 13 solid diethyldithiophosphinates. For dimethyl and diethyldithiophosphates the preferred conformation is (*ap,ap*), while the diethyldithiophosphinates have a more varied pattern: (*ap,ap*), (*ap,sc*) and in some cases (*sc,sc*). A plausible reason may be found in back-donation of the lone pair on oxygen into phosphorus π-orbitals, making the P–O bond in the dithiophosphates more rigid than the P–C bond in the dithiophosphinates, where back-donation does not occur. The conformational variation among the dithiophosphinates is also shown by the relatively large number of disordered ligands in these compounds. The (*ap,sc*) conformation is common in disordered ligands and ligands acting as bridges, as is the case in **1** and **2**.

Changing the substituent on phosphorus often leads to changes in the structure. Compound **1** is best described as a PS_4 pyramid with Pb in one corner and two S atoms from other ligands at rather long distances on the remaining "free" Pb side. These S atoms are involved in weak interactions with the Pb atoms. The closely related compound $Pb[S_2P(OC_2H_5)_2]_2$[10] has a similar Pb coordination, but the two additional S atoms are at much longer distances, 3.469 (6) and 3.478(6) Å. In $Pb[S_2P(CH(CH_3)_2)_2]_2$[9] the Pb coordination polyhedron is a pentagonal bipyramid with a lone pair in the equatorial plane formed by four almost planar equatorial Pb–S bonds from two bidentate ligands. As indicated by the discussion in the previous section, a rather distorted picture emerges if pentagonal bipyramids are used to describe the coordination about Pb in compound **1**: the equatorial planes are not formed by bidentate ligands, cf. Figs. 1 and 2.

The influence of the R group is also clearly seen from the puckering of the eight-membered ring formed, e.g., in compound **2**. The ring puckering will be described with parameters calculated according to Cremer and Pople[24] and Evans and Boyens.[25] For an eight-membered ring five parameters are needed, three amplitudes (q_2, q_3 and q_4) and two phase angles (φ_2 and φ_3). They are defined by eqns. (1) and (2), where $m = 2$ and 3 is given by eqn. (3) for q_4.

$$q_m \cos \varphi_m = (1/4)^{1/2} \sum_j z_j \cos [2\pi m(j-1)/n] \quad (1)$$

$$q_m \sin \varphi_m = (1/4)^{1/2} \sum_j z_j \sin [2\pi m(j-1)/n] \quad (2)$$

$$q_4 = (1/8)^{1/2} \sum_j (-1)^{j-1} z_j \quad (3)$$

The quantity z_j is the distance to the mean plane satisfying $\Sigma_j z_j = 0$. In order to plot the five parameters in two dimen-

Table 6. Torsion angles (see Fig. 11 for definition of angles *a–h*) and puckering parameters[24,25] for $M_2[S_2PR_2]_4$ compounds forming eight-membered rings. The ligands are *A* = $S_2P(OCH(CH_3)_2)_2$, *B* = $S_2P(C_2H_5)_2$ and *C* = $S_2P(C_3H_7)_2$.

M R	Mn[26] *B*	Zn[27] *B*	Zn[28] *C*	Zn[8] *A*	Cd[8] *A*	Cd[a] *B*
a/°	−95.3(1)	−33.5(4)	−119.3(1)	27.4(4)	30.7(5)	−92.63(9)
b/°	11.6(1)	77.0(5)	37.1(1)	−79.1(3)	−86.4(5)	11.5(1)
c/°	76.3(1)	17.4(6)	40.7(1)	−10.5(4)	−0.9(5)	78.3(1)
d/°	−156.4(1)	−79.8(5)	−122.4(1)	75.2(3)	72.8(4)	−150.64(9)
e/°	95.3(1)	−25.8(4)	119.3(1)	27.4(4)	30.7(5)	92.63(9)
f/°	−11.6(1)	76.2(7)	−37.1(1)	−79.1(4)	−86.4(5)	−11.5(1)
g/°	−76.3(1)	12.4(7)	−40.7(1)	−10.5(4)	−0.9(5)	−78.3(1)
h/°	156.3(1)	−71.3(5)	122.4(1)	75.2(3)	72.8(4)	150.64(9)
q_2/Å	0.0	2.700	0.0	2.658	2.805	0.0
q_3/Å	1.871	0.053	1.693	0.0	0.0	1.925
θ/°	90.0	91.7	90.0	88.2	87.3	90.0
φ_2/°	138.4	114.2	142.6	295.7	296.9	148.9
φ_3/°	350.1	343.7	359.3	328.2	329.7	349.9
Type[25]	TC 0	S 10	TC 0	S 6	S 6	TC 0

[a]Compound **2**.

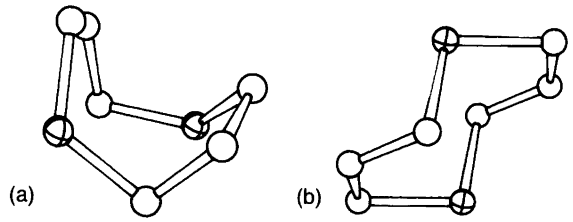

Fig. 10. The two conformations found among the eight-membered rings: (a) saddle, S; (b) twisted chair, TC.

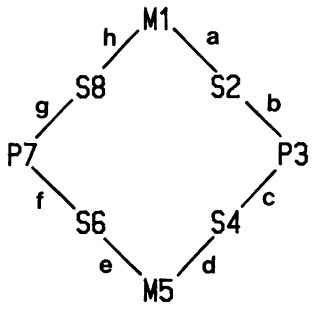

Fig. 11. The torsion angle notation *a–h* used for the eight-membered rings in Table 6.

sions the number of amplitudes is reduced by introducing a third angular parameter θ such that $\cos\theta = q_4/(\Sigma_j z_j^2)^{1/2}$. The torsion angles and the puckering parameters for six compounds forming eight-membered rings are shown in Table 6. There are two groups of ring conformations, saddle (S) and twisted chair (TC). They are depicted in Fig. 10. The twisted chair conformation is a result of a centre of symmetry while a twofold axis leads to the saddle, but no other rule indicating which ring conformation should be expected has been found.

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