Table 3. *Least-squares planes and deviations* (Å) *of atoms from the planes*

E.s.d.'s are *ca* 0·01 Å and 0·2°.

Plane (1): O(1) 0·09, N(1) −0·09, O(1*) −0·09, N(1*) 0·09
Plane (2): Mn −0·03, O(1) 0·08, N(1) −0·02, C(1) 0·00, C(2) −0·07, C(11) 0·04
Plane (3): Mn, N(1), N(1*) 0·00, C(12)† 0·32

The plane containing atoms C(n), n = 1 to 10 inclusive is planar within experimental error: it makes an angle of 20·3° with plane (2). The two symmetry-related metallocycles intersect at 11·8°.

† Atom not contributing to the plane.

1·416 (15) and 1·426 (15) Å, and the angle between the planes of the metallocycle is 11·8 (1)° (Table 3), compared to 4·8° in the four-coordinate structure of [NiL] (Akhtar, 1981), 6·0° in [CuL^1(dmso)$_{0·5}$] and 37·1° in [NiL^1] (Akhtar & Drew, 1982). The [NiL] and [CuL^1(dmso)$_{0·5}$] structures contain centrosymmetric dimers with Ni···Ni 3·324 and Cu···Cu 3·613 Å whereas the [NiL^1] complex exists as monomers (closest Ni–Ni distance is 4·07 Å). Thus the angle between the metallocycle rings is decreased by metal···metal interaction and the resulting steric repulsion between adjacent ligands. The effect of the polymer formation is not so restrictive but keeps the angle well below the value found in [NiL^1], which we take to be an unstrained value. The average distance in the naphthyl ring is 1·403 Å which is close to expected values. The sum of the bond angles around the N atom is 359·5° indicating the trigonal nature of the bonding. The angle at the C atoms of the ethylenediamine groups is 107·5 (9)° showing tetrahedral configuration. The ethylene C atoms are displaced by 0·32 Å from the coordination plane (Table 3) indicating a symmetrical

gauche form and the torsion angle around the —CH$_2$—CH$_2$— bond is 47·2 (1)°; these values are similar to those observed for some ethylenediamine complexes (Davies, Gatehouse & Murray, 1973; Shkol'nikova, Yumal, Shugam & Voblikova, 1970; Llewellyn & Waters, 1960; Scouloudi, 1953).

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Bis(di-*n*-propyldithiophosphinato)zinc(II)

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Abstract. [Zn{(*n*-C$_3$H$_7$)$_2$PS$_2$}$_2$], C$_{12}$H$_{28}$P$_2$S$_4$Zn, triclinic, P$\bar{1}$, a = 8·409 (5), b = 9·771 (6), c = 13·451 (7) Å, α = 90·99 (5), β = 99·28 (4), γ = 105·27 (5)°, Z = 2, D_x = 1·35 Mg m^{-3}, M_r = 427·9, μ(Mo $K\alpha$) = 1·72 mm^{-1}; final R = 0·057 for 3111 X-ray data. The complex forms dimers with point symmetry $\bar{1}$. The endocyclic dithiophosphinato groups link the Zn atoms into an eight-membered ring while the exocyclic groups function as chelating ligands. Their geometry is affected by a disorder which can be described by split-atom positions of one S atom and of the *n*-propyl groups.

Introduction. A review on the preparation of dithiophosphinato complexes has been given by Kuchen &

Hertel (1969). A colorless crystal approximately $0.2 \times 0.3 \times 0.3$ mm showing ill defined faces was used for data collection and determination of the lattice parameters (12 reflections, Mo $K\alpha$ radiation, $25 < 2\theta < 28°$). Photographs yielded the Laue group $\bar{1}$; the space group $P\bar{1}$ containing one $[\mathrm{Zn}\{(n\text{-}\mathrm{C}_3\mathrm{H}_7)_2\mathrm{PS}_2\}_2]$ formula unit as the asymmetric unit was confirmed by the structure determination. The intensities of all symmetry-independent reflections up to $2\theta = 58°$ (Mo $K\alpha$ radiation, crystal monochromator, ω scan) were measured with an automated diffractometer (Syntex $P2_1$). Three reflections with too-high intensities had to be eliminated; the final set of data contained 5585 reflections, of which 3111 were classified observed $(I > 1.96\sigma_I)$ and used for the determination and refinement of the structure. No absorption correction has been applied $(\mu = 1.72$ mm^{-1}). Initial atomic coordinates of five heavy atoms could be obtained from the Patterson function. The structure was completed in the usual way. During early stages of the refinement the C atoms of the exocyclic di-*n*-propyldithiophosphinato group showed an unreasonable geometry and unusually high temperature factors up to $B_{ii} = 48$ Å^2, indicating incorrect symmetry or disorder. Thus, the symmetry was reduced using the space group $P1$ and one dimer as the asymmetric unit. However, the refinement did not converge satisfactorily; the corresponding B values still ranged up to $B_{ii} = 38$ Å^2 and the reduction of the R factor was not significant according to Hamilton's (1974) test. Alternatively, disorder had to be considered. An analysis of the B values indicated a disorder of the atom S(2) perpendicular to the plane of the ring defined by the atoms Zn, S(1), S(2), and P(2). If atoms Zn, S(1), and P(2) (all with reasonable B values) were held fixed this disorder would cause an additional disorder of the adjacent *n*-propyl groups. Further refinement was achieved with split-atom positions of the atom S(2) and the six C atoms of the *n*-propyl groups with occupancy factors of 0.5. The final refinement including H atoms of the endocyclic *n*-propyldithiophosphinato group converged at $R = 0.057$ (0.112) and $R_w = 0.057$ (0.065), respectively, for the observed (all) reflections. Weights were derived from counting statistics by $1/w = \sigma_F^2 + (0.02F)^2$; scattering factors were taken from Cromer & Waber (1974), those of the atoms Zn, S, and P being corrected for anomalous dispersion. The final parameters of the non-H atoms are listed in Table 1.* The anisotropic temperature factors of the unsplit atoms are in the usual range; those of the disordered positions show values up to 22 Å^2. All calculations were carried out on

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, non-bonded distances, and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36349 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters of the non-*H *atoms with e.s.d.'s in parentheses*

S atoms labelled with two and the C atoms with three digits are split-atom positions. The equivalent isotropic temperature factors are calculated by $B_{eq} = \frac{1}{3}(B_{11}\,a^{*2}\,a^2 + B_{12}\,a^*\,b^*\,ab\cos\gamma + \ldots)$.

	x	y	z	B_{eq} (Å^2)
Zn(1)	0.02960 (7)	0.04756 (6)	0.14384 (4)	4.26 (2)
S(1)	−0.2227 (2)	−0.1169 (2)	0.1598 (1)	5.63 (4)
S(21)	0.0655 (20)	0.0793 (12)	0.3274 (11)	7.14 (28)
S(22)	0.0588 (19)	0.1260 (12)	0.3215 (11)	6.14 (21)
S(3)	0.2647 (2)	−0.0133 (1)	0.1126 (1)	5.97 (5)
S(4)	0.0395 (2)	0.2502 (2)	0.0549 (1)	5.83 (5)
P(1)	0.1769 (2)	−0.2077 (1)	0.0424 (1)	4.15 (4)
P(2)	−0.1564 (2)	−0.0415 (2)	0.3048 (1)	6.55 (5)
C(11)	0.344 (1)	−0.231 (1)	−0.019 (1)	5.1 (2)
C(12)	0.312 (1)	−0.373 (1)	−0.075 (1)	7.0 (3)
C(13)	0.458 (1)	−0.387 (1)	−0.123 (1)	8.8 (4)
C(14)	0.140 (1)	−0.343 (1)	0.132 (1)	5.3 (2)
C(15)	0.286 (1)	−0.335 (1)	0.216 (1)	7.7 (2)
C(16)	0.246 (1)	−0.449 (1)	0.290 (1)	10.6 (3)
C(211)	−0.208 (4)	−0.198 (5)	0.381 (1)	10.3 (11)
C(212)	−0.096 (5)	−0.178 (3)	0.384 (1)	8.9 (8)
C(221)	−0.118 (6)	−0.287 (4)	0.373 (2)	11.6 (12)
C(222)	−0.275 (4)	−0.315 (3)	0.375 (2)	12.2 (9)
C(231)	−0.155 (5)	−0.408 (4)	0.449 (3)	13.1 (15)
C(232)	−0.238 (7)	−0.440 (5)	0.432 (4)	17.5 (18)
C(241)	−0.336 (2)	0.057 (2)	0.315 (1)	6.2 (5)
C(242)	−0.297 (2)	0.004 (2)	0.369 (2)	7.6 (6)
C(251)	−0.303 (2)	0.125 (3)	0.419 (1)	8.8 (7)
C(252)	−0.331 (3)	0.144 (3)	0.328 (3)	12.8 (13)
C(261)	−0.427 (3)	0.188 (4)	0.432 (3)	9.7 (10)
C(262)	−0.484 (3)	0.185 (5)	0.394 (3)	10.8 (11)

an Eclipse computer (Data General) with a local modified version of the EXTL system (Syntex).

Discussion. For investigations of concentration- and temperature-dependent molecular association by vapor-pressure osmometry, Mamsch (1981) selected the title compound as a suitable model. As proposed by Kuchen, Metten & Judat (1964) an equilibrium of monomers and dimers in solution could be proved. However, ^{31}P NMR spectra at lower temperature showed splitting of lines, which raised the question of conformeric molecules of the dimers. To gain further information this X-ray study has been undertaken. Crystal structures of a few zinc complexes containing dialkyl residues have been reported: a dithiophosphinate, $[\mathrm{Zn}\{(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{PS}_2\}_2]$ (Calligaris, Nardin & Ripamonti, 1970), forms discrete dimers, while a dithiophosphate, $[\mathrm{Zn}\{(\mathrm{OC}_2\mathrm{H}_5)_2\mathrm{PS}_2\}_2]$ (Ito, Igarashi & Hagihara, 1969), a monothiophosphinate, $[\mathrm{Zn}\{(n\text{-}\mathrm{C}_4\mathrm{H}_9)_2\mathrm{PSO}\}_2]$ (Calligaris, Ciana, Meriani, Nardin, Randaccio & Ripamonti, 1970), and a phosphinate, $[\mathrm{Zn}\{(n\text{-}\mathrm{C}_4\mathrm{H}_9)(\mathrm{C}_6\mathrm{H}_5)\mathrm{PO}_2\}_2]$ (Giordano, Randaccio & Ripamonti, 1969), all form polymers.

Fig. 1 shows two formula units with bond lengths; main bond angles are given in Table 2. The molecules form discrete dimers by the catenation of the dithiophosphinato groups and Zn atoms while the remaining

$R_2PS_2^-$ group chelates the Zn atom. By the dimerization *via* a crystallographic center of symmetry a puckered eight-membered ring is formed which has a chair conformation [atoms S(3), P(1), S(4)^a, S(4), P(1)^a, and S(3)^a are coplanar within 0·01 Å; symmetry code (*a*) $-x,-y,-z$]; torsion angles have been deposited.* The bonding angles within the ring vary from 102·3 (1)° at the Zn atom to 118·2 (1)° at P(1). The latter value exceeds the tetrahedron angle significantly and is comparable to the average value of 115·4 (3)° found for the diethyldithiophosphinato anion (Meyer, Mootz & Wunderlich, 1981). The average bond lengths within the ring are Zn—S 2·314 (2) and P—S 2·004 (2) Å and agree with values from the literature. With respect to the atoms of the ring, there are a few short non-bonded distances less than 3·9 Å which enlarge the coordination sphere of the Zn atom and may cause an additional distortion of the tetrahedral geometry of the Zn atom (see Table 2).

The chelating dithiophosphinato group forms a four-membered ring with increased Zn—S distances.
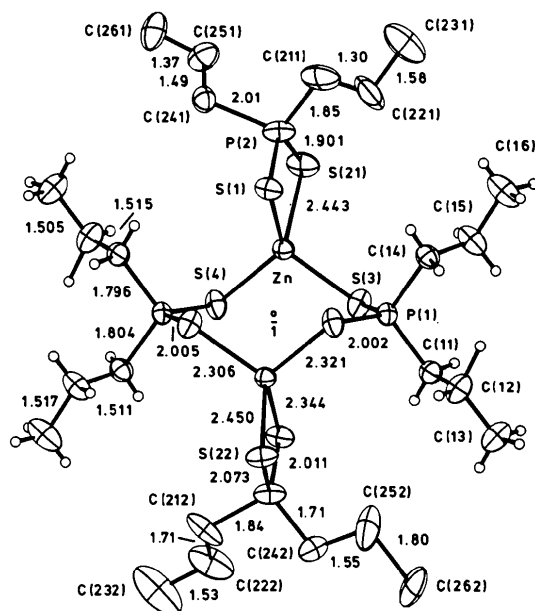
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* See deposition footnote.

Fig. 1. The dimer of [Zn{(*n*-C₃H₇)₂PS₂}₂] in arbitrary crystallographic orientation with point symmetry Ī. The positional disorder of the exocyclic dialkyldithiophosphinato group is described by alternative split-atom positions which are shown separately in the upper half (last digit of numbering 1) and in the lower half (last digit 2) respectively. Thus, the figure containing two molecules in alternative disordered positions does not reveal exactly the point symmetry Ī. The geometry of the disordered C atoms is strongly affected by the disorder. The non-H atoms are represented by thermal ellipsoids of 25% probability (*ORTEP* II, Johnson, 1976). The radius of the H atoms was set to $B = 1·0$ Å². The e.s.d.'s are: Zn—S and P—S 0·002, P—C 0·007, C—C 0·010–0·015 Å. Participation of split-atom positions increases these values by a factor of ~6.

Table 2. *Bond angles* (°)

Angles between the alternative atoms of the disordered positions are not reported.

(i) Angles at the Zn atom

The e.s.d.'s are 0·1° without participation of split-atom positions and 0·3–0·5° otherwise.

	S(1)	S(21)	S(22)	S(3)
S(21)	84·1			
S(22)	88·4			
S(3)	124·3	105·2	111·3	
S(4)	122·5	116·5	105·5	102·3

(ii) Remaining angles within or at the eight-membered ring

The e.s.d.'s are 0·1–0·3°. Symmetry code: (*a*) $-x,-y,-z$.

Zn—S(3)—P(1)	104·6	S(3)—P(1)—C(11)	104·6
Zn—S(4)—P(1)^a	105·6	S(3)—P(1)--C(14)	111·2
S(3)—P(1)—S(4)^a	118·2	S(4)^a—P(1)—C(11)	111·2
C(11)—P(1)—C(14)	107·6	S(4)^a· P(1)—C(14)	103·9

(iii) Remaining angles within the four-membered ring

The e.s.d.'s are 0·1° at S(1) and 0·4–0·6° otherwise.

Zn—S(1)—P(2)	82·7	S(1)—P(2)—S(21)	110·0
Zn—S(21)—P(2)	82·3	S(1)—P(2)—S(22)	109·8
Zn—S(22)—P(2)	78·8		

(iv) Angles involving the *n*-propyl groups. The alternative split-atom positions are identified by *n* = 1 and *n* = 2.

The e.s.d.'s are 0·5–0·8° at atoms with first index of labelling equal to 1 and 1–3° otherwise.

P(1)—C(11)—C(12)	115·8	P(1)—C(14)—C(15)	115·0
C(11)—C(12)—C(13)	113·5	C(14)—C(15)—C(16)	112·5

	n = 1	*n* = 2			*n* = 1	*n* = 2
S(1)—P(2)—C(21*n*)	106	110		P(2)—C(21*n*)—C(22*n*)	114	105
S(1)—P(2)—C(24*n*)	100	121		C(21*n*)—C(22*n*)—C(23*n*)	111	110
S(2*n*)—P(2)—C(21*n*)	119	105		P(2)—C(24*n*)—C(25*n*)	108	109
S(2*n*)—P(2)—C(24*n*)	115	109		C(24*n*)—C(25*n*)—C(26*n*)	110	107
C(21*n*)—P(2)—C(24*n*)	105	101				

The two split-atom positions S(21) and S(22) are separated from each other by 0·48 (2) Å and are 0·18 (1) and 0·27 (1) Å, respectively from the plane defined by Zn, S(1), and P(2). However, these split-atom positions of S(2) and those of the *n*-propyl groups should be regarded as a description of the disorder only. As can be seen from the orientation of the thermal ellipsoids (Fig. 1), as well as from the unusual geometry within the *n*-propyl groups, this disorder is clearly not a two-positional one. Obviously, these atoms are fixed at all intermediate positions during the crystallization of the molecules, thus simulating a dynamic disorder. This interpretation is underlined by a difference electron density map calculated with the final parameters but excluding the split atoms. There is a remarkable electron density in the area between the corresponding atom positions. By geometric criteria the split atoms could be attached very clearly to the alternative *n*-propyl groups (see Fig. 1). The distances between the split C atoms vary between 0·64 (7) and 1·28 (7) Å.* Similar disorder is indicated by the high temperature factors in the structures of the Zn complexes cited above. The endocyclic *n*-propyldithiophosphinate

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* See deposition footnote.

group is well located and does not show any unusual structural features.

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Structure of Phenyltellurium Trichloride

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Abstract. [Te(C_6H_5)]Cl_3, $M_r = 311 \cdot 07$, triclinic, $P\bar{1}$, $a = 16 \cdot 687$ (3), $b = 8 \cdot 616$ (2), $c = 7 \cdot 471$ (1) Å, $\alpha = 90 \cdot 79$ (2), $\beta = 114 \cdot 18$ (1), $\gamma = 112 \cdot 30$ (2)°, $V = 888 \cdot 21$ Å^3, $Z = 4$ (with two independent molecules in the asymmetric unit), $D_c = 2 \cdot 326$, $D_o = 2 \cdot 33$ Mg m^{-3}. 2661 observed [$I \geq 2 \cdot 3 \, \sigma(I)$] reflections were used in the refinement and gave a final discrepancy index of $R = 0 \cdot 025$. The structure is polymeric with bridging Cl atoms; each Te atom lies in an octahedral environment surrounded by four Cl atoms, a C atom and a lone pair of electrons.

Introduction. The literature contains a number of crystallographic studies of alkyl- and aryltellurium trihalides (Kobelt & Paulus, 1971; McCullough & Knobler, 1976; McCullough, 1977; Knobler & McCullough, 1977; Bergman & Engman, 1979). The tellurium halide skeletal structures of these compounds are all, to some extent, different, showing varying degrees of halogen bridging.

At present, it is unclear which are the factors which influence these crystal structures. Therefore, to improve present information on $RTeX_3$ compounds, we now report the structure of PhTeCl$_3$. This compound was of further interest in connection with previous vibrational spectroscopic studies (McWhinnie & Thavornyuti-karn, 1972) on phenyltellurium trihalides in which a

dimeric structure (PhTeX_3)$_2$ containing bridging halogen atoms was proposed for chloro and iodo derivatives and some kind of polymeric arrangement was inferred for the bromo compound.

Precession and Weissenberg photographs were used to determine approximate cell dimensions and the diffraction symbol for the crystals. A suitable crystal (0·18 × 0·16 × 0·25 mm) for data collection was mounted in a Lindemann capillary and accurate cell dimensions were determined by least-squares refinement of 20 accurately measured reflections ($2\theta = 28$–35°, Mo $K\alpha$ radiation). Data were collected at 293 K using a Picker FACS-I four-circle diffractometer [λ(Mo $K\alpha$) = 0·70926 Å] with a graphite monochromator and a scintillation detector with pulse-height discrimination. The take-off angle was 3° and a symmetrical θ–2θ scan (2° min^{-1}) of (1·6 + 0·692 tan θ)° was used. Stationary-crystal stationary-counter background counts of 10% of the scan time were taken at each side of the scan. A peak profile analysis was performed on each reflection and the intensity and its associated error determined by the method of Grant & Gabe (1977). Intensity measurements of two standards every 70 reflections showed no evidence of crystal deterioration and no instability of the detection system.

Intensities were measured for 3129 independent reflections ($2\theta \leq 50°$), of which 2661 were classed observed [$I \geq 2 \cdot 3\sigma(I)$]. Lorentz, polarization and

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