

SHORT-FORMAT PAPERS

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Structure of Bis(diethyldithiophosphinato)cadmium(II)

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Abstract. $[\text{Cd}\{(\text{C}_2\text{H}_5)_2\text{PS}_2\}_2]$, $M_r = 418.9$, orthorhombic, $Pbca$, $a = 12.066$ (1), $b = 20.320$ (2), $c = 13.813$ (2) Å, $V = 3386.7$ (7) Å³, $Z = 8$, $D_m = 1.6$, $D_x = 1.64$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.91$ mm⁻¹, $F(000) = 1680$, room temperature, $R = 0.050$ for 2499 unique observed reflections. The complex forms dimers about a crystallographic center of symmetry containing an eight-membered ring of endocyclic dithiophosphinato groups and Cd atoms. In addition, every Cd atom is chelated by an exocyclic diethyldithiophosphinato group whose geometry is affected by a disorder of one S atom and of the ethyl groups.

Experimental. The title compound has been prepared by Mamsch (1981) according to Kuchen, Metten & Judat (1964). The crystallization from chloroform yielded large crystals containing cavities and inclusions of the solvent; a recrystallization from butanol gave well shaped transparent crystals. Photographs showed orthorhombic symmetry and the systematic absences of the space group $Pbca$. Crystal of approx. $0.5 \times 0.3 \times 0.3$ mm used for data collection and determination of lattice constants (Mo $K\alpha$, 15 reflections, $30 < 2\theta < 34^\circ$). Density, determined by flotation, yielded $Z = 8$ formula units per cell. Intensities of all 3693 symmetry-independent reflections up to $(\sin\theta)/\lambda = 0.64$ Å⁻¹ (Mo $K\alpha$, Syntex $P2_1$, crystal monochromator) measured with an ω scan of 0.6° and variable scan speeds between 1.5 and $58^\circ \text{ min}^{-1}$. Indices ranged from 0 to $h = 15$, $k = 25$, and $l = 17$. Three standard reflections (7,11,3, 359, 3,13,6) monitored every 200 reflections did not vary significantly. 257 reflections showed imbalances of the backgrounds of more than 3:2 and have been corrected by replacing the higher background by the lower one. Possibly, these data are affected by multiple reflections. A comparison

of the backgrounds of these reflections with those of neighboring reflections as well as ψ scans of a few selected reflections support this view. In one example, the intensity of the reflection 038 is reduced from 133σ , to zero by a ψ scan.* No absorption correction has been applied due to the low absorption coefficient. 2518 reflections with $I > 1.96\sigma$, classified 'observed' and used for structure determination and primary refinement. At a later stage 20 reflections showing too-high values of F_o and asymmetric profiles of the scan (probably caused by multiple reflections) were eliminated. The final set of data contained 2499 observed out of 3673 reflections.

* See deposition footnote.

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{Å}^2)$
Cd	0.01219 (4)	0.09502 (2)	0.04137 (3)	4.59 (1)
S(1)	0.1667 (2)	0.1028 (1)	0.1652 (1)	5.86 (5)
S(21)	-0.0303 (3)	0.2115 (1)	0.1130 (3)	5.48 (10)
S(22)	-0.0443 (3)	0.2028 (2)	0.1428 (3)	6.91 (12)
S(3)	0.0248 (1)	0.1148 (1)	-0.1407 (1)	4.96 (4)
S(4)	-0.1538 (1)	0.0185 (1)	0.0469 (1)	4.38 (4)
P(1)	-0.1353 (1)	-0.0417 (1)	0.1625 (1)	4.10 (4)
P(2)	0.0980 (2)	0.1893 (1)	0.2052 (1)	5.60 (5)
C(11)	-0.0939 (6)	0.0043 (3)	0.2682 (5)	5.5 (2)
C(12)	-0.0977 (8)	-0.0330 (4)	0.3630 (5)	8.0 (3)
C(13)	-0.2705 (5)	-0.0760 (3)	0.1864 (5)	5.7 (2)
C(14)	-0.3144 (6)	-0.1196 (4)	0.1094 (7)	7.7 (3)
C(211)	0.1906 (12)	0.2552 (8)	0.2130 (9)	6.5 (4)
C(212)	0.2102 (12)	0.2563 (6)	0.1779 (10)	5.7 (4)
C(221)	0.2336 (14)	0.2656 (7)	0.1079 (12)	8.9 (6)
C(222)	0.2597 (13)	0.2608 (10)	0.0781 (11)	8.7 (6)
C(231)	0.0274 (15)	0.1790 (8)	0.3281 (11)	8.0 (6)
C(232)	0.0985 (16)	0.1971 (7)	0.3441 (11)	8.2 (6)
C(241)	0.0980 (24)	0.1423 (12)	0.3901 (12)	14.3 (11)
C(242)	0.0333 (19)	0.1437 (9)	0.3923 (15)	11.4 (8)

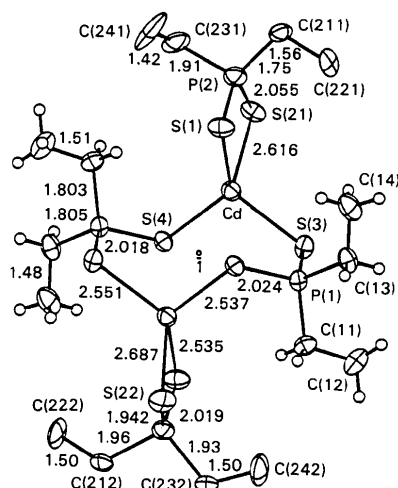


Fig. 1. One dimer of $[\text{Cd}\{(\text{C}_2\text{H}_5)_2\text{PS}_2\}_2]$ formed *via* a crystallographic center of symmetry. The disorder of the exocyclic diethylthiophosphinato group is represented by alternative split-atom positions which are shown separately on the left (last digit of numbering 1) and on the right (last digit 2). Thus, the figure does not reveal exactly the point symmetry $\bar{1}$ of the dimer. The non-H atoms are represented by thermal ellipsoids of 25% probability (ORTEP, Johnson, 1976). The radius of the H atoms was set to $B = 1.5 \text{ \AA}^2$. The e.s.d.'s of the bond lengths (\AA) are: Cd-S 0.002, S-P 0.002, P-C 0.007, and C-C 0.01. Participation of split-atom positions increases these values by a factor of ≈ 2 .

Table 2. Bond angles ($^\circ$)

(a) Angles at the Cd atom; e.s.d.'s are 0.06° and are approximately doubled with participation of split-atom positions

	S(1)	S(21)	S(22)	S(3)
S(21)	80.32			
S(22)	77.51			
S(3)	127.70	104.03	113.63	
S(4)	126.77	112.86	106.45	99.98

(b) Remaining angles within or at the eight-membered ring; e.s.d.'s are $0.1\text{--}0.3^\circ$; symmetry code: (i) $-x, -y, -z$

Cd-S(3)-P(1)	94.1	C(11)-P(1)-S(4 ⁱ)	110.9
Cd-S(4)-P(1)	107.9	C(11)-P(1)-C(13)	107.6
S(3)-P(1)-S(4 ⁱ)	113.6	C(13)-P(1)-S(3)	109.9
C(11)-P(1)-S(3)	108.6	C(13)-P(1)-S(4 ⁱ)	106.2

(c) Remaining angles within the four-membered ring; e.s.d.'s are $0.1\text{--}0.2^\circ$

Cd-S(1)-P(2)	86.4	P(2)-S(21)-Cd	83.6
S(1)-P(2)-S(21)	109.3	P(2)-S(22)-Cd	83.8
S(1)-P(2)-S(22)	111.4		

Table 3. Torsion angles ($^\circ$) of the eight-membered ring compared with idealized values of a chair conformation (Hendrickson, 1967)

For the angles of the opposite bonds the signs have to be changed.

Bonds	S(4)-Cd	Cd-S(3)	S(3)-P(1)	P(1)-S(4 ⁱ)
Torsion angle	150.2	-93.7	11.9	76.9
Ideal chair	119.9	-76.2	0	76.2

Initial coordinates of the Cd atom obtained from Patterson function, and structure completed in usual way. Unusually high temperature factors (up to $B_{ii} = 33 \text{ \AA}^2$) within the exocyclic diethylthiophosphinato group accompanied by an unreasonable geometry indicated disorder. This problem was treated by split-atom positions (occupancy factors 0.5) of one S atom and the two ethyl groups as in the analogous complex $[\text{Zn}\{(n\text{-C}_3\text{H}_7)_2\text{PS}_2\}_2]$ (Wunderlich, 1982). H atoms of the endocyclic diethylthiophosphinato group localized from a difference electron density map and included with fixed atom parameters. Final refinement on F performed using block-diagonal method. All 181 parameters converged with $\Delta/\sigma < 0.14$ at $R = 0.050(0.077)$ and $wR = 0.059(0.063)$ for observed(all) data at minimum of $S = 1.67$. Weights according to $w = 1/(\sigma_F^2 + 0.0004F^2)$ used; scattering factors from Cromer & Waber (1974) with corrections for anomalous dispersion of atoms Cd, S and P (Cromer & Liberman, 1974). Residual electron density ranged from -0.67 to $+0.45 \text{ e \AA}^{-3}$. The final parameters of the refined atoms are listed in Table 1.* All calculations were performed with a local modified version of the program system *EXTL* (Syntex). Fig. 1 shows one dimer of the complex with bond lengths. As can be seen from the high anisotropy of the thermal parameters of the disordered atoms the disorder is clearly not a two-positional one and has to be interpreted in the same way as in the Zn complex cited above. Main bond angles are listed in Table 2. A comparison of the torsion angles within the central eight-membered ring with idealized values (Hendrickson, 1967) of a chair conformation is given in Table 3 and indicates a distorted chair conformation for the eight-membered heterocyclic ring.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and an appendix to the *Experimental* have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42681 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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