Refinement

Refinement on F^2
$R(F) = 0.0370$
$wR(F^2) = 0.1118$
$S = 1.113$
7489 reflections
339 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.4257P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.042$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni1	0	0	0	0.03853 (9)
N2	−0.0151 (2)	0.1403 (2)	0.13140 (11)	0.0465 (4)
C3	0.0319 (3)	0.1341 (3)	0.2170 (2)	0.0663 (6)
C4	0.0130 (3)	0.2488 (3)	0.2865 (2)	0.0679 (7)
C5	0.0476 (4)	0.2934 (5)	0.3908 (2)	0.118 (2)
N6	−0.0472 (2)	0.3254 (2)	0.24223 (14)	0.0663 (5)
C7	−0.0636 (3)	0.2563 (2)	0.1491 (2)	0.0580 (5)
N8	0.2275 (2)	0.0438 (2)	0.04806 (12)	0.0456 (4)
C9	0.3003 (2)	−0.0279 (2)	0.0917 (2)	0.0540 (5)
C10	0.4450 (2)	0.0490 (2)	0.1220 (2)	0.0537 (5)
C11	0.5694 (3)	0.0229 (4)	0.1730 (2)	0.0790 (8)
N12	0.4613 (2)	0.1710 (2)	0.09562 (14)	0.0607 (5)
C13	0.3303 (2)	0.1637 (2)	0.0522 (2)	0.0566 (5)
N14	−0.0475 (2)	−0.1809 (2)	0.05014 (13)	0.0508 (4)
C15	−0.0767 (2)	−0.2677 (2)	0.08593 (14)	0.0464 (4)
N16	−0.0921 (2)	−0.3612 (3)	0.1316 (2)	0.0783 (7)
C17	−0.2168 (3)	−0.4587 (2)	0.1235 (2)	0.0567 (5)
N18	−0.3175 (3)	−0.5503 (3)	0.1215 (2)	0.0937 (8)
Ni19	1/2	0	1/2	0.03534 (8)
N20	0.3782 (2)	−0.1425 (2)	0.36880 (11)	0.0426 (3)
C21	0.4243 (2)	−0.2377 (2)	0.29782 (15)	0.0509 (5)
C22	0.3106 (3)	−0.3190 (2)	0.2275 (2)	0.0566 (5)
C23	0.3009 (4)	−0.4357 (4)	0.1361 (2)	0.0986 (11)
N24	0.1921 (2)	−0.2723 (2)	0.25571 (13)	0.0589 (5)
C25	0.2368 (2)	−0.1668 (2)	0.3404 (2)	0.0542 (5)
N26	0.5393 (2)	0.1796 (2)	0.45108 (12)	0.0454 (4)
C27	0.4417 (3)	0.2218 (3)	0.4018 (2)	0.0571 (5)
C28	0.5119 (3)	0.3427 (3)	0.3812 (2)	0.0596 (6)
C29	0.4585 (4)	0.4331 (4)	0.3313 (2)	0.0943 (11)
N30	0.6561 (2)	0.3741 (2)	0.4180 (2)	0.0664 (5)
C31	0.6674 (3)	0.2745 (2)	0.4591 (2)	0.0622 (6)
N32	0.6976 (2)	−0.0440 (2)	0.45719 (13)	0.0492 (4)
C33	0.7844 (2)	−0.0990 (2)	0.4283 (2)	0.0479 (4)
N34	0.8906 (2)	−0.1515 (2)	0.3949 (2)	0.0857 (8)
C35	0.8835 (2)	−0.2888 (2)	0.3804 (2)	0.0523 (5)
N36	0.8910 (3)	−0.4064 (2)	0.3662 (2)	0.0692 (6)

Table 2. *Selected geometric parameters (Å, °)*

Ni1—N2	2.090 (2)	Ni19—N26	2.090 (2)
Ni1—N14	2.114 (2)	Ni19—N20	2.107 (2)
Ni1—N8	2.115 (2)	Ni19—N32	2.120 (2)
N14—C15	1.140 (2)	N32—C33	1.135 (2)
C15—N16	1.304 (3)	C33—N34	1.305 (3)
N16—C17	1.291 (3)	N34—C35	1.294 (3)
C17—N18	1.127 (3)	C35—N36	1.141 (3)
N2—Ni1—N14	89.81 (7)	N26—Ni19—N20	90.71 (7)
N2—Ni1—N8	87.89 (7)	N26—Ni19—N32	90.62 (7)
N14—Ni1—N8	89.25 (7)	N20—Ni19—N32	90.67 (7)
C15—N14—Ni1	172.2 (2)	C33—N32—Ni19	164.8 (2)
N14—C15—N16	172.6 (2)	N32—C33—N34	175.2 (2)
C17—N16—C15	122.0 (2)	C35—N34—C33	120.6 (2)
N18—C17—N16	172.8 (3)	N36—C35—N34	173.5 (2)

Non-H atoms were refined anisotropically. H atoms were refined as riding on their parent C/N atoms and five parameters were refined per methyl group. The crystal was bounded by the faces (0$\bar{1}$0), (010), (1$\bar{1}$1), ($\bar{1}$1$\bar{1}$), (10$\bar{1}$), (00$\bar{1}$) and (1$\bar{1}$0). The structure was solved by Patterson methods and refined on F^2 by least-squares methods.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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8-[1,2-Bis(diphenylphosphino)ethane]-9,10-μ-hydrido-8-rhoda-7-thia-*nido*-undecaborane(10)–Dichloromethane (2/1)

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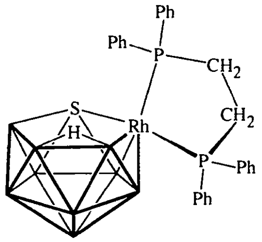
Abstract

The solid-state structure of the title compound, $[Rh(B_9H_{10}S)(C_{26}H_{24}P_2)].0.5CH_2Cl_2$, has a *nido* cluster geometry but, apparently, only a *closo* electron count. This anomaly is rationalized in terms of long range *ortho*-phenyl agostic C—H···Rh interactions.

Comment

The anomalous geometries in some 11-vertex metallathiaboranes (Ferguson *et al.*, 1990; Murphy, Spalding, Ferguson & Gallagher, 1992; Adams, McGrath & Welch, 1995) have been recently investigated. The compounds display a *nido* molecular geometry, while possessing a cluster electron count more consistent with that of a *closo* species (Wade, 1976). We have reported previously (Adams, McGrath & Welch, 1995) the synthesis of 8-($Ph_2P—CH_2CH_2—PPh_2$)-9,10-μ-H-8,7-*nido*-$RhSB_9H_{10}$, an 11-vertex thiaborane which has a *nido* molecular architecture [13 skeletal electron pairs (s.e.p.'s)], but only a *closo* electron count (12 s.e.p.'s). To explain this anomaly, we identified (Adams, McGrath, Thomas, Weller & Welch, 1996) two one-electron long-range agostic C—H···Rh interactions (Brookhart & Green, 1983; Brookhart, Green & Wong, 1988) furnishing the metal centre, and thus the cluster overall, with an additional two electrons (total 13 s.e.p.'s). Through this additional interaction, the observed *nido* structure is now fully consistent with the theoretical prediction (Wade, 1976).

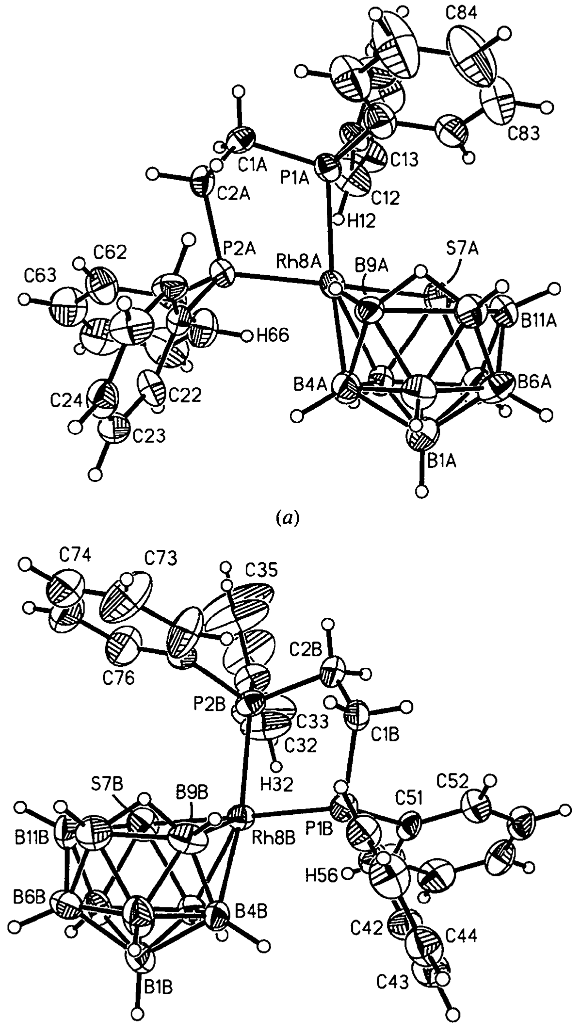
The title compound, (I), crystallizes with no crystallographically imposed symmetry and no close intermolecular contacts. Two independent molecules (*A* and *B*) crystallize in the asymmetric unit. One molecule of dichloromethane solvent co-crystallizes with the two metallathiaborane molecules.



(I)

Perspective views of both molecules, with the atomic numbering schemes adopted, are shown in Figs. 1(*a*) and 1(*b*). As with the previously reported crystalline form [α form, rhodathiaborane–CH_2Cl_2 (1/2)], the title complex is an 11-vertex $RhSB_9$ polyhedron displaying a gross *nido*-cage geometry. The Rh8—S7 distances are 2.351 (3) and 2.364 (4) Å in the two independent molecules, compared with 2.366 (2) Å in the α form. In both the crystalline forms, the Rh—B and S—B distances are essentially similar. The cage B—B separations, lying in the ranges 1.70 (2)–1.90 (2) and 1.69 (2)–1.91 (2) Å for molecules *A* and *B*, respectively, compared with 1.730 (12)–1.879 (11) Å for the α form.

The environment of the Rh atom in both molecules is distorted, with the RhP_2 plane non-orthogonal to the metal-bonded SB_3 plane [dihedral angles of 57.8 (4) and 56.7 (3)° in molecules *A* and *B*, respectively] and with a vacant metal coordination site *trans* to B9. Two *ortho*-H atoms, one from each PPh_2 fragment [H12 and H66 (molecule *A*); H32 and H56 (molecule *B*)] are located *ca* 3 Å from the Rh metal atoms [Rh8*A*···H12 3.254 (11) and Rh8*A*···H66 2.742 (12); Rh8*B*···H32 3.119 (14) and Rh8*B*···H56 2.849 (10) Å], with the midpoint of the pairs of H atoms essentially occupying the vacant coordination site. This is the same situation as found in the α form, in which the *ortho*-phenyl Rh···H—C interactions were measured as 3.174 and 2.809 Å.



(*a*)

(*b*)

Fig. 1. Perspective views of (*a*) molecule *A* and (*b*) molecule *B* of 8-[1,2-bis(diphenylphosphino)ethane]-9,10-μ-hydrido-8-rhoda-7-thia-*nido*-undecaborane(10)–dichloromethane (2/1), with 40% probability displacement ellipsoids, except for H atoms which have artificial radii of 0.1 Å for clarity.

The fact that the complex in this new crystalline form also displays two close *ortho*-phenyl Rh···H—C interactions further supports the rationalization of the apparently anomalous structures of this family of compounds.

Experimental

Crystals of the title compound were formed by prolonged exposure (one week) of $[1,1\text{-dppe-}1,2\text{-}RhSB_9H_9][PhCH_2NMe_3]$ (Adams, McGrath, Thomas, Weller & Welch, 1996) to CH_2Cl_2 in a CH_2Cl_2/petroleum ether (60–80) solution at 243 K [dppe is 1,2-bis(diphenylphosphino)ethane]. The title compound is thus formed by protonation of the anion, the proton source being the solvent.

Crystal data

$[Rh(B_9H_{10}S)(C_{26}H_{24}P_2)]_2$.-
CH_2Cl_2
$M_r = 1366.38$
Orthorhombic
$Pna2_1$
$a = 36.429\ (3)$ Å
$b = 10.7030\ (10)$ Å
$c = 16.5300\ (10)$ Å
$V = 6445.0\ (9)$ Å^3
$Z = 4$
$D_x = 1.406$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 35 reflections
$\theta = 4.577\text{–}12.416°$
$\mu = 0.795$ mm^{-1}
$T = 293\ (2)$ K
Block
0.30 × 0.25 × 0.20 mm
Yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (*SHELXTL*/*PC*; Sheldrick, 1994)
$T_{\min} = 0.518$, $T_{\max} = 0.643$
7000 measured reflections
6087 independent reflections

4694 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0476$
$\theta_{\max} = 25°$
$h = -1 \rightarrow 43$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 19$
3 standard reflections monitored every 97 reflections
intensity decay: 5.48%

Refinement

Refinement on F^2
$R(F) = 0.0529$
$wR(F^2) = 0.1406$
$S = 1.104$
6060 reflections
631 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 11.1945P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -1.441$ (Flack parameter)

$\Delta\rho_{\max} = 0.595$ e Å^{-3}
$\Delta\rho_{\min} = -0.766$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.11 (8)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Rh8*A*	−0.48425 (2)	−0.54207 (8)	0.0239 (2)	0.0357 (2)
S7*A*	−0.48850 (9)	−0.7267 (3)	−0.0525 (3)	0.0450 (7)
P1*A*	−0.43286 (8)	−0.6037 (3)	0.0971 (3)	0.0380 (6)
P2*A*	−0.47536 (8)	−0.3559 (3)	0.0848 (3)	0.0357 (6)
C1*A*	−0.4124 (3)	−0.4658 (12)	0.1427 (7)	0.039 (3)
C2*A*	−0.4426 (3)	−0.3737 (11)	0.1673 (8)	0.041 (3)
B1*A*	−0.5666 (5)	−0.6070 (17)	−0.0666 (10)	0.054 (4)
B2*A*	−0.5385 (5)	−0.7377 (16)	−0.0977 (11)	0.057 (4)
B3*A*	−0.5196 (4)	−0.5740 (13)	−0.0836 (8)	0.041 (3)
B4*A*	−0.5436 (4)	−0.5011 (14)	−0.0007 (10)	0.050 (4)
B5*A*	−0.5733 (4)	−0.6127 (14)	0.0381 (10)	0.049 (4)
B6*A*	−0.5691 (4)	−0.7540 (17)	−0.0159 (10)	0.053 (4)
B9*A*	−0.5326 (4)	−0.5789 (13)	0.0930 (10)	0.044 (3)
B10*A*	−0.5496 (4)	−0.7445 (15)	0.0812 (10)	0.049 (4)
B11*A*	−0.5270 (4)	−0.8207 (14)	−0.0063 (10)	0.048 (3)
C11	−0.3955 (2)	−0.6819 (8)	0.0449 (5)	0.042 (2)
C12	−0.3907 (2)	−0.6607 (9)	−0.0374 (5)	0.069 (5)
C13	−0.3615 (3)	−0.7154 (11)	−0.0781 (5)	0.071 (5)
C14	−0.3369 (2)	−0.7912 (10)	−0.0365 (6)	0.077 (5)
C15	−0.3416 (2)	−0.8124 (10)	0.0458 (6)	0.086 (5)
C16	−0.3709 (3)	−0.7578 (10)	0.0865 (4)	0.075 (5)
C21	−0.5120 (2)	−0.2575 (6)	0.1276 (4)	0.037 (2)
C22	−0.5304 (2)	−0.1747 (7)	0.0771 (4)	0.049 (3)
C23	−0.5577 (2)	−0.0977 (7)	0.1083 (5)	0.047 (3)
C24	−0.5665 (2)	−0.1035 (7)	0.1900 (5)	0.051 (3)
C25	−0.5481 (2)	−0.1863 (9)	0.2405 (4)	0.057 (4)
C26	−0.5208 (2)	−0.2633 (7)	0.2093 (4)	0.044 (3)
C61	−0.4526 (2)	−0.2518 (7)	0.0130 (5)	0.045 (3)
C62	−0.4385 (3)	−0.1367 (8)	0.0367 (5)	0.061 (4)
C63	−0.4228 (3)	−0.0576 (7)	−0.0203 (7)	0.077 (5)
C64	−0.4212 (3)	−0.0935 (10)	−0.1010 (6)	0.082 (6)
C65	−0.4353 (3)	−0.2086 (11)	−0.1248 (4)	0.083 (6)
C66	−0.4510 (3)	−0.2877 (8)	−0.0677 (5)	0.063 (4)
C81	−0.4462 (3)	−0.7100 (8)	0.1792 (5)	0.055 (3)
C82	−0.4599 (3)	−0.8261 (8)	0.1569 (5)	0.055 (3)
C83	−0.4736 (3)	−0.9068 (8)	0.2155 (7)	0.087 (6)
C84	−0.4735 (4)	−0.8713 (10)	0.2964 (7)	0.112 (9)
C85	−0.4597 (4)	−0.7552 (11)	0.3187 (5)	0.126 (11)
C86	−0.4461 (3)	−0.6745 (8)	0.2601 (6)	0.081 (5)
Rh8*B*	−0.26836 (2)	0.31564 (8)	−0.45258 (7)	0.0352 (2)
S7*B*	−0.21102 (9)	0.3869 (3)	−0.5012 (2)	0.0554 (9)
P1*B*	−0.32417 (8)	0.2615 (3)	−0.4058 (2)	0.0370 (6)
P2*B*	−0.30055 (9)	0.4055 (3)	−0.5576 (2)	0.0395 (7)
C1*B*	−0.3566 (3)	0.2679 (12)	−0.4898 (7)	0.043 (3)
C2*B*	−0.3506 (3)	0.3840 (14)	−0.5406 (8)	0.050 (3)
B1*B*	−0.1905 (4)	0.1735 (18)	−0.3821 (10)	0.056 (4)
B2*B*	−0.1719 (4)	0.2860 (18)	−0.4486 (12)	0.062 (4)
B3*B*	−0.2148 (4)	0.3142 (17)	−0.3844 (10)	0.051 (3)
B4*B*	−0.2401 (4)	0.1709 (14)	−0.3787 (8)	0.042 (3)
B5*B*	−0.2157 (5)	0.0595 (16)	−0.4357 (12)	0.065 (5)
B6*B*	−0.1768 (4)	0.1326 (18)	−0.4832 (11)	0.062 (4)
B9*B*	−0.2554 (4)	0.1227 (12)	−0.4789 (11)	0.050 (3)
B10*B*	−0.2160 (5)	0.1011 (19)	−0.5415 (11)	0.063 (5)
B11*B*	−0.1872 (4)	0.2458 (18)	−0.5507 (11)	0.059 (4)
C31	−0.2957 (3)	0.5721 (7)	−0.5737 (6)	0.056 (3)
C32	−0.2817 (4)	0.6430 (10)	−0.5103 (5)	0.088 (6)
C33	−0.2755 (4)	0.7702 (9)	−0.5208 (7)	0.133 (11)
C34	−0.2833 (5)	0.8263 (7)	−0.5947 (8)	0.117 (9)
C35	−0.2972 (5)	0.7554 (10)	−0.6581 (6)	0.182 (18)
C36	−0.3034 (4)	0.6283 (10)	−0.6476 (6)	0.120 (10)
C41	−0.3336 (2)	0.1127 (6)	−0.3534 (4)	0.040 (3)
C42	−0.3294 (2)	0.1078 (6)	−0.2699 (4)	0.047 (3)
C43	−0.3369 (3)	−0.0024 (8)	−0.2284 (4)	0.064 (4)
C44	−0.3485 (2)	−0.1076 (6)	−0.2705 (6)	0.059 (4)
C45	−0.3526 (2)	−0.1027 (6)	−0.3541 (6)	0.063 (4)
C46	−0.3452 (2)	0.0074 (7)	−0.3955 (4)	0.049 (3)
C51	−0.3404 (2)	0.3783 (7)	−0.3343 (5)	0.038 (3)
C52	−0.3773 (2)	0.3872 (7)	−0.3135 (5)	0.048 (3)
C53	−0.3886 (2)	0.4746 (8)	−0.2565 (5)	0.055 (4)
C54	−0.3630 (2)	0.5530 (8)	−0.2203 (5)	0.058 (4)
C55	−0.3261 (2)	0.5441 (8)	−0.2411 (5)	0.066 (4)
C56	−0.3148 (2)	0.4567 (9)	−0.2981 (5)	0.055 (3)
C71	−0.2890 (2)	0.3307 (8)	−0.6527 (5)	0.047 (3)
C72	−0.3067 (3)	0.2218 (9)	−0.6765 (6)	0.081 (6)
C73	−0.2955 (3)	0.1596 (9)	−0.7461 (7)	0.106 (8)
C74	−0.2666 (3)	0.2064 (11)	−0.7919 (5)	0.080 (5)
C75	−0.2489 (3)	0.3153 (12)	−0.7680 (6)	0.087 (6)
C76	−0.2601 (3)	0.3775 (9)	−0.6984 (6)	0.081 (5)
Cl2†	−0.3786 (3)	−0.0738 (10)	−0.7822 (6)	0.152 (3)§
Cl1*A*†	−0.3872 (4)	0.0386 (14)	−0.6300 (8)	0.210 (5)§
C100	−0.3858 (12)	−0.108 (3)	−0.682 (2)	0.28 (3)§
Cl1*B*‡	−0.3467 (13)	−0.059 (5)	−0.627 (2)	0.18 (2)§

† Site occupancy = 0.90. ‡ Site occupancy = 0.20. § $U_{\rm iso}$.

Table 2. *Selected geometric parameters (Å, °)*

Rh8A—B3A	2.221 (14)	Rh8B—B3B	2.255 (15)
Rh8A—B4A	2.244 (14)	Rh8B—B4B	2.226 (14)
Rh8A—B9A	2.13 (2)	Rh8B—B9B	2.163 (14)
Rh8A—S7A	2.351 (3)	Rh8B—S7B	2.364 (4)
Rh8A—P1A	2.324 (3)	Rh8B—P1B	2.251 (3)
Rh8A—P2A	2.256 (3)	Rh8B—P2B	2.305 (3)
S7A—B2A	1.97 (2)	S7B—B2B	1.99 (2)
S7A—B3A	2.053 (15)	S7B—B3B	2.09 (2)
S7A—B11A	1.89 (2)	S7B—B11B	1.92 (2)
P1A—C1A	1.817 (12)	P1B—C1B	1.825 (12)
P1A—C11	1.817 (6)	P1B—C51	1.819 (6)
P1A—C81	1.837 (7)	P1B—C41	1.845 (6)
P2A—C2A	1.822 (12)	P2B—C2B	1.860 (13)
P2A—C21	1.841 (6)	P2B—C31	1.812 (8)
P2A—C61	1.827 (7)	P2B—C71	1.813 (7)
C1A—C2A	1.53 (2)	C1B—C2B	1.52 (2)
B1A—B2A	1.81 (2)	B1B—B2B	1.77 (3)
B1A—B3A	1.77 (2)	B1B—B3B	1.75 (2)
B1A—B4A	1.78 (2)	B1B—B4B	1.81 (2)
B1A—B5A	1.75 (2)	B1B—B5B	1.76 (3)
B1A—B6A	1.78 (3)	B1B—B6B	1.80 (2)
B2A—B3A	1.90 (2)	B2B—B3B	1.91 (2)
B2A—B6A	1.76 (2)	B2B—B6B	1.75 (3)
B2A—B11A	1.80 (2)	B2B—B11B	1.83 (3)
B3A—B4A	1.80 (2)	B3B—B4B	1.79 (2)
B4A—B5A	1.74 (2)	B4B—B5B	1.76 (2)
B4A—B9A	1.80 (2)	B4B—B9B	1.82 (2)
B5A—B6A	1.76 (2)	B5B—B6B	1.80 (2)
B5A—B9A	1.78 (2)	B5B—B9B	1.75 (2)
B5A—B10A	1.80 (2)	B5B—B10B	1.81 (3)
B6A—B10A	1.76 (2)	B6B—B10B	1.75 (2)
B6A—B11A	1.70 (2)	B6B—B11B	1.69 (2)
B9A—B10A	1.89 (2)	B9B—B10B	1.78 (3)
B10A—B11A	1.85 (2)	B10B—B11B	1.88 (3)
B9A—Rh8A—B3A	85.5 (6)	B9B—Rh8B—B3B	84.6 (6)
B9A—Rh8A—B4A	48.6 (6)	B9B—Rh8B—B4B	49.1 (6)
B3A—Rh8A—B4A	47.6 (6)	B3B—Rh8B—B4B	47.1 (6)
B9A—Rh8A—P2A	92.4 (4)	B9B—Rh8B—P2B	110.9 (4)
B3A—Rh8A—P2A	125.2 (4)	B3B—Rh8B—P2B	145.1 (4)
B4A—Rh8A—P2A	92.7 (4)	B4B—Rh8B—P2B	159.9 (4)
B9A—Rh8A—P1A	109.5 (4)	B9B—Rh8B—P1B	91.2 (4)
B3A—Rh8A—P1A	147.1 (4)	B3B—Rh8B—P1B	127.5 (4)
B4A—Rh8A—P1A	157.8 (4)	B4B—Rh8B—P1B	92.9 (4)
P1A—Rh8A—P2A	84.43 (11)	P1B Rh8B—P2B	84.65 (12)
B9A—Rh8A—S7A	94.5 (4)	B9B—Rh8B—S7B	92.7 (4)
B3A—Rh8A—S7A	53.3 (4)	B3B—Rh8B—S7B	53.6 (4)
B4A—Rh8A—S7A	90.2 (4)	B4B—Rh8B—S7B	90.1 (4)
P2A—Rh8A—S7A	172.70 (13)	P2B—Rh8B—S7B	93.38 (13)
P1A—Rh8A—S7A	95.41 (12)	P1B—Rh8B—S7B	176.09 (13)
B11A—S7A—B2A	55.6 (7)	B11B—S7B—B2B	55.7 (8)
B11A—S7A—B3A	96.6 (6)	B11B—S7B—B3B	97.5 (8)
B2A—S7A—B3A	56.2 (7)	B2B—S7B—B3B	56.0 (7)
B11A—S7A—Rh8A	106.2 (5)	B11B—S7B—Rh8B	106.8 (5)
B2A—S7A—Rh8A	108.4 (5)	B2B—S7B—Rh8B	108.1 (5)
B3A—S7A—Rh8A	60.1 (4)	B3B—S7B—Rh8B	60.5 (4)
C1A—P1A—C11	105.3 (5)	C1B—P1B—C51	104.9 (5)
C1A—P1A—C81	107.7 (5)	C1B—P1B—C41	105.6 (5)
C11—P1A—C81	105.3 (4)	C41—P1B—C51	103.2 (4)
C1A—P1A—Rh8A	108.4 (4)	C1B—P1B—Rh8B	108.3 (4)
C11—P1A—Rh8A	119.2 (3)	C41—P1B—Rh8B	123.5 (3)
C81—P1A—Rh8A	110.4 (4)	C51—P1B—Rh8B	109.9 (3)
C2A—P2A—C61	104.6 (5)	C2B—P2B—C71	107.7 (5)
C2A—P2A—C21	104.3 (5)	C2B—P2B—C31	103.9 (6)
C61—P2A—C21	103.3 (4)	C31—P2B—C71	106.5 (5)
C2A—P2A—Rh8A	109.6 (4)	C2B—P2B—Rh8B	109.5 (4)
C61—P2A—Rh8A	108.3 (3)	C71—P2B—Rh8B	110.5 (3)
C21—P2A—Rh8A	124.9 (3)	C31—P2B—Rh8B	118.1 (4)
C2A—C1A—P1A	109.8 (7)	C2B—C1B—P1B	111.0 (9)
C1A—C2A—P2A	109.8 (8)	C1B—C2B—P2B	109.1 (9)
B11A—B2A—S7A	59.9 (8)	B11B—B2B—S7B	60.4 (8)
B3A—B2A—S7A	64.1 (7)	B3B—B2B—S7B	64.6 (7)
B2A—B3A—S7A	59.7 (7)	B2B—B3B—S7B	59.4 (7)
B4A—B3A—Rh8A	66.9 (6)	B4B—B3B—Rh8B	65.6 (7)
S7A—B3A—Rh8A	66.6 (4)	S7B—B3B—Rh8B	65.9 (5)
B3A—B4A—Rh8A	65.5 (7)	B3B—B4B—Rh8B	67.3 (7)
B9A—B4A—Rh8A	62.5 (6)	B9B—B4B—Rh8B	63.7 (6)
B4A—B9A—Rh8A	68.9 (7)	B4B—B9B—Rh8B	67.3 (7)
B10A—B9A—Rh8A	112.9 (9)	B10B—B9B—Rh8B	114.5 (9)
B9A—B10A—B11A	110.4 (10)	B9B—B10B—B11B	112.9 (13)
B2A—B11A—S7A	64.5 (8)	B2B—B11B—S7B	64.0 (8)
B10A—B11A—S7A	114.3 (9)	B10B—B11B—S7B	111.2 (10)
C12—C11—P1A	118.8 (5)	C32—C31—P2B	117.6 (6)
C16—C11—P1A	121.1 (5)	C36—C31—P2B	122.4 (6)
C22—C21—P2A	118.9 (4)	C42—C41—P1B	118.6 (4)
C26—C21—P2A	121.1 (4)	C46—C41—P1B	121.4 (4)
C62—C61—P2A	121.6 (5)	C52—C51—P1B	121.5 (4)
C66—C61—P2A	118.3 (5)	C56—C51—P1B	118.5 (4)
C82—C81—P1A	117.0 (5)	C72—C71—P2B	120.5 (5)
C86—C81—P1A	122.8 (5)	C76—C71—P2B	119.3 (5)

H atoms attached to B atoms were located from $\Delta\rho$ maps and allowed positional refinement subject to a common B—H distance; 1.10 (5) Å for terminal H atoms and 1.20 (5) Å for bridging H atoms at convergence. All B-bound H atoms were assigned fixed isotropic displacement parameters ($U_{\rm iso}$ = 0.08 Å^2). The phenyl H atoms were constrained to idealized positions (C—H 0.93 Å) as were the methylene H atoms (C—H 0.97 Å). The isotropic displacement parameters of both of these sets of H atoms were defined as 1.2$U_{\rm iso}$ of their bound C atoms. The phenyl rings were constrained to an idealized geometry (C—C = 1.390 Å and C—C—C = 120°). In the C31–C35 phenyl ring, however, there is significant vibration perpendicular to the plane of the ring. The CH_2Cl_2 solvent was disordered, with one postion found for the C atom and three for the Cl atoms, to which fixed occupancies were assigned (0.9, 0.9 and 0.2) to give approximately equal refined $U_{\rm iso}$ values. H atoms were not included in the solvent model. All solvent atom displacement parameters were refined isotropically. The Flack (1983) χ parameter was refined to −0.11 (8) and no consistent relationship was found between the coordinates of the heavy atoms, thus *Pna*2$_1$ was adopted as the correct space group for this structure.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1398). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Linear-Chain Structure of Bis(*O*,*O*′-dimethyldithiophosphato)cadmium(II)

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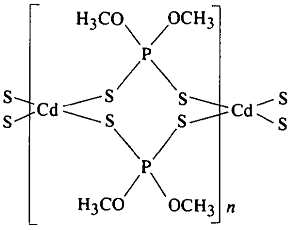
Abstract

The two ligands in the title compound, *catena*-poly[cadmium-μ-bis(O,O'-dimethyldithiophosphato-S:S')], $[Cd\{S_2P(OCH_3)_2\}_2]$, bridge two adjacent Cd atoms forming a linear chain along the *c* axis. The chain has a twofold symmetry axis through the Cd atoms. The Cd atom is coordinated by four S atoms in a distorted tetrahedral arrangement. The Cd—S bond lengths are 2.565 (2) and 2.571 (2) Å.

Comment

Metal dialkyl dithiophosphates, $[M\{S_2P(OCH_3)_2\}_n]$, are an interesting group of complexes which show various kinds of coordination around metals and various modes of molecular aggregation (Lawton & Kokotailo, 1969; Ito, Igarashi & Hagihara, 1969; Ito, 1972). We report here the crystal structure of $[Cd\{S_2P(OCH_3)_2\}_2]$, (I), which displays a distorted tetrahedral coordination and a linear-chain structure.



(I)

An *ORTEP*II drawing (Johnson, 1976) of the structure of (I) with the atomic numbering scheme is shown in Fig. 1. The linear-chain structure is similar to that in zinc diethyl dithiophosphate (Ito *et al.*, 1969), but in the latter, one ligand is bridging and the other is chelating. On the other hand, zinc and cadmium diisopropyl dithiophosphates are both dimeric (Lawton & Kokotailo, 1969). The Cd atom lies on a twofold axis and has distorted tetrahedral coordination of four S atoms. The Cd—S1 and Cd—S2 bond lengths are 2.565 (2) and 2.571 (2) Å, respectively. The S—Cd—S angles range from 102.34 (4) to 124.23 (7)°.

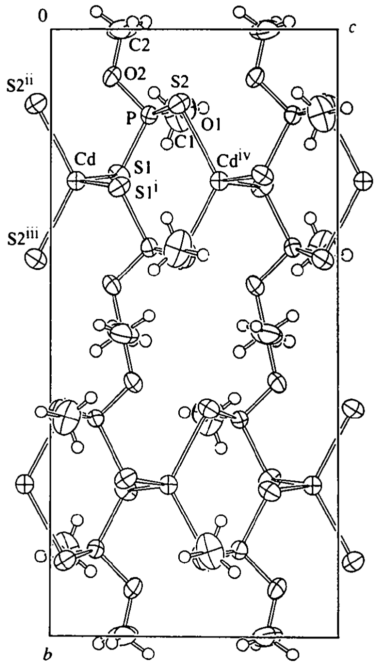


Fig. 1. The crystal structure viewed down the *a* axis (*ORTEP*II; Johnson, 1976). The displacement ellipsoids are at the 50% probability level. Symmetry codes: (i), (ii), (iii) as in Table 1; (iv) $x, \frac{1}{2} - y, z + \frac{1}{2}$.

Experimental

Powdered P_2S_5 (0.05 mol) was added to 70 ml of CH_3OH and heated to 323–333 K. After ~1 h, when the generation of H_2S vapour ceased, powdered $CdSO_4$ (0.05 mol) was added to the solution to give a white precipitate of $[Cd\{S_2P(OCH_3)_2\}_2]$. Colourless crystals were obtained by recrystallization of the precipitate from an acetone solution.

Crystal data

$[Cd(C_2H_6O_2PS_2)_2]$
$M_r = 426.72$
Orthorhombic
Pccn
$a = 9.282\ (4)$ Å
$b = 17.837\ (5)$ Å
$c = 8.488\ (4)$ Å
$V = 1405.2\ (9)$ Å^3
$Z = 4$
$D_x = 2.017$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 24–25°$
$\mu = 2.336$ mm^{-1}
$T = 295$ K
Needle
0.80 × 0.20 × 0.20 mm
Colourless