C(2)—C(3)—C(4)	112,9 (12)	C(8)—C(9)—Hg(4)	107,2 (10)
C(2)—C(3)—Hg(1)	110,7 (11)	C(10)—C(9)—Hg(3)	111,8 (11)
C(2)—C(3)—Hg(2)	108,5 (10)	C(10)—C(9)—Hg(4)	109,9 (11)
C(4)—C(3)—Hg(1)	110,9 (10)	Hg(3)—C(9)—Hg(4)	104,2 (7)

La structure obtenue rend compte d'une dimercuration des molécules d'acétoacétate d'éthyle *via* les atomes de C des groupements méthylènes en α des deux fonctions carbonyles. Les distances Hg—C et Hg—Cl observées sont en accord avec les valeurs trouvées dans le cas de structures de même type décrites dans la littérature. Des contacts Hg···O sont mis en évidence à l'intérieur de l'unité asymétrique. De tels contacts peuvent expliquer les faibles écarts à la linéarité observés dans le cas des enchainements C—Hg—Cl. Une molécule d'acétonitrile (CH_3CN) est également présente dans l'unité asymétrique.

L'enregistrement a été effectué à l'aide d'un diffractomètre équipé d'un monochromateur en graphite: balayage $\Delta\omega = (0{,}80 + 0{,}34\tan\theta)^\circ$, vitesse variable de 1,8 à 20,1° $\min^{-1}$ en ω en fonction de l'intensité du pic de diffraction.

Les atomes Hg et Cl ont été localisés par les méthodes directes à l'aide du programme *SHELXS*86 (Sheldrick, 1985). La structure a été résolue par des synthèses de Fourier différence successives et affinements par moindres carrés en matrice totale, en utilisant le programme *CRYSTALS* (Watkin, Carruthers & Betteridge, 1988), adapté sur un micro-ordinateur Dell 333D (processeur 80386, 33MHz). Une correction d'absorption a été appliquée après l'affinement isotrope de tous les atomes. Les coordonnées des atomes d'H ont été calculées. Leurs positions ont été introduites dans l'affinement et un facteur d'agitation thermique commun a été affiné. Au total, 262 paramètres variables ont été considérés: facteur d'échelle, facteur d'extinction secondaire (Larson, 1970), coordonnées atomiques, facteurs d'agitation thermique, isotrope pour les atomes d'H et anisotropes pour les autres atomes.

Deux positions statistiques pour les atomes C(6) et C(6') ont été observées par Fourier différence. Leurs taux d'occupation, x et $(1 - x)$, et un facteur d'agitation thermique commun, ont été affinés. On trouve pour C(6) $x = 0{,}67$ et pour C(6') $(1 - x) = 0{,}33$. Sur la Fig. 1, seul C(6) a été représenté.

Les listes des facteurs de structure, des facteurs d'agitation déplacement anisotrope, des coordonnées des atomes d'hydrogène, et des distances et angles des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71608: 29 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU1049]

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Acta Cryst. (1994). C**50**, 367-369

A Zirconium Polyhydride Dimer, $[Zr_2H_4(BH_4)_4(PMe_3)_4]$

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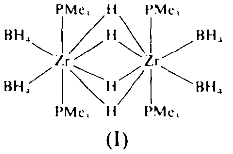
(*Received* 24 *February* 1993; *accepted* 30 *July* 1993)

Abstract

The dimer tetra-μ-hydrido-bis[bis(tetrahydroborato)-bis(trimethylphosphine)zirconium(IV)], $[Zr(BH_4)_2H_2(C_3H_9P)_2]_2$, consists of two Zr atoms linked by four bridging hydride ligands. Each Zr atom is ligated by two PMe_3 ligands and two bidentate BH_4 groups. The single crystallographically independent Zr atom lies on a twofold axis and the molecule has exact $\bar{4}$ point symmetry.

Comment

The title compound (I) was prepared by the reaction of $Zr(BH_4)_4$ (James & Smith, 1974) with 16 equivalents of PMe_3 in pentane at 195 K. On warming to room temperature, the initially formed white precipitate dissolved and then decomposed to yield green crystals suitable for X-ray structure analysis (typical yield 14%).



(I)

The Zr···Zr contact distance of 2.979 (1) Å is significantly shorter than that seen in the related triple-hydride-bridged dimer $[Zr_2H_3(BH_4)_5(PMe_3)_2]$, where Zr···Zr is 3.124 (1) Å (Gozum & Girolami, 1991). This is consistent with the shortening of the Zr···Zr contact distance observed on increasing the number of bridging hydrides between the metal centres as seen on comparing the triple-bridged dimer $[Zr_2H_3(BH_4)_5(PM_3)_2]$ and the double-bridged dimer $[Cp_2'ZrH_2]_2$, where Zr···Zr is 3.460 (1) Å (Jones & Petersen, 1981). The Zr···B contact distance of 2.59 (1) Å is similar to that of the η^2-BH_4^- group in $[Zr_2H_3(BH_4)_5(PMe_3)_2]$ [Zr···B = 2.604 (8) Å] and is indicative of an η^2- rather than an η^3-BH_4^- group (Edelstein, 1981).

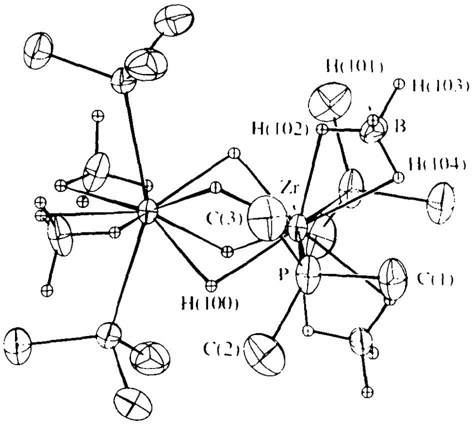


Fig. 1. *SNOOPI* (Davies & Prout, 1981) plot of the molecular structure of the title compound.

Experimental

Crystal data

$[Zr_2H_4(BH_4)_4(C_3H_9P)_4]$
M_r = 550.16
Tetragonal
$P4/n$ (origin on $\bar{1}$)
a = 13.516 (7) Å
c = 10.353 (5) Å
V = 1891.3 Å^3
Z = 2
D_x = 0.967 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 10.5-15°
μ = 0.707 mm^{-1}
T = 296 K
Cuboid
0.456 × 0.380 × 0.380 mm
Deep green

Data collection

Stoe Stadi-4 diffractometer
Learnt profile scans
Absorption correction: empirical
T_{min} = 0.533, T_{max} = 0.616
2076 measured reflections
1674 independent reflections
874 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0214
θ_{max} = 25°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity variation: −15%

Refinement

Refinement on F
R = 0.062
wR = 0.054
S = 1.82
874 reflections
65 parameters
Weights based on third-order Chebyshev polynomial in F_c

$(\Delta/\sigma)_{max}$ = 0.1
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Atomic scattering factors from *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985)

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

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

	x	y	z	U_{eq}
Zr	3/4	1/4	0.14389 (7)	0.0559
P	0.8791 (2)	0.3992 (2)	0.2049 (2)	0.0790
C(1)	0.903 (1)	0.417 (1)	0.374 (1)	0.1045
C(2)	0.8434 (9)	0.5227 (8)	0.149 (1)	0.1172
C(3)	1.0011 (9)	0.381 (1)	0.134 (1)	0.1174
B	0.6307 (9)	0.3608 (8)	0.275 (1)	0.0805

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

Zr···Zr^i	2.979 (1)	Zr—H(100)	2.08*
Zr—P	2.740 (3)	Zr^i—H(100)	2.10*
Zr—B	2.59 (1)	Zr—H(102)	2.16 (5)
P—C(1)	1.80 (1)	Zr—H(104)	2.20 (5)
P—C(3)	1.82 (1)	P—C(2)	1.83 (1)
P—Zr—P^{ii}	153.4 (1)	Zr^i···Zr—B	121.6 (3)
B—Zr—B^{ii}	116.7 (6)	Zr—H(100)—Zr^i	91*
Zr^i···Zr—P	103.32 (5)		

Symmetry codes: (i) $\frac{1}{2} + y, -x, -z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, z$.

* No e.s.d. value as H-atom position was not refined.

The crystal was sealed in an 0.5 mm capillary tube under nitrogen using Apiazon N grease to prevent movement. The standard intensities decreased steadily during the data collection to a minimum of around 85% of their original values, probably as a result of deterioration of the crystal in the X-ray beam. The structure was solved by Patterson interpretation using the program *SHELXS*86 (Sheldrick, 1985) and also by Fourier synthesis. The structure was refined using the program *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Initially, the non-H atom positions and anisotropic temperature factors were refined, followed by difference Fourier synthesis to locate the H atoms. Two of the H atoms bonded to B and the single independent bridging hydride were located; the remaining H atoms were generated automatically. The H-atom positions were refined as part of rigid methyl or BH_4 groups or with the C or B atom as the pivot atom. The methyl groups were additionally constrained to maintain regular tetrahedral coordination with respect to the P—C bond by fixing two of the P—C—H bond angles. The isotropic temperature factors of the H atoms were also refined, constraining the values for all methyl H atoms and all boron hydride H atoms to be equal. The position and temperature factor of the bridging hydride were not refined.

The weighting scheme used was $w = w'[1-(\Delta F/\Delta F_{est})^2]^2$, where $w' = 1/[A[0]T[0]'(X) + A[1]T[1]'(X) + A[2]T[2]'(X)]$, a third-order Chebyshev polynomial in $T[i]'$ with coefficients $A[i]$ ($A[0] = 263$, $A[1] = 371$, $A[2] = 122$) and $X = F_c/F_{c(max)}$. ΔF_{est} in the initial equation is obtained from the Chebyshev fit.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond lengths around pivot atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71529 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1053]

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Acta Cryst. (1994). C**50**, 369–371

Dichloro[5,8-dimethyl-1,12-di-2-pyrrolyl-2,5,8,11-tetraaza-1,11-dodecadiene-N^2,N^5,N^8,N^{11}]cadmium(II)

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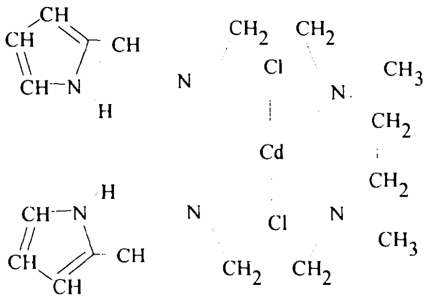
(*Received* 22 *March* 1993; *accepted* 13 *July* 1993)

Abstract

In $[Cd(C_{18}H_{28}N_6)Cl_2]$ the Cd atom is located on a twofold rotation axis and is octahedrally coordinated by two Cl atoms [Cd—Cl 2.533 (3) Å], two azomethine N atoms [Cd—N(2) 2.45 (1) Å] and two amino N atoms [Cd—N(1) 2.458 (9) Å] in a distorted geometry. The pyrrole N atoms are not coordinated.

Comment

The application of an electrochemical procedure to the synthesis of metal complexes with Schiff bases has been the object of several papers from our laboratory. Starting from the metal as the anode of an electrolytic cell, the synthesis of metal-pyrrolaldiminates has been described (Castro, Romero, García-Vázquez, Durán, Sousa, Castellano & Zukerman-Schpector, 1992). We have now applied the same method to the synthesis of the complex dichloro[5,8-dimethyl-1,12-di-2-pyrrolyl)-2,5,8,11-tetraaza-1,11-dodecadiene]cadmium(II) (I), and determined its structure by X-ray diffraction.



(I)

Fig. 1 shows the title molecule and the numbering scheme applied. The coordination polyhedron around the metal atom can be described as a distorted octahedron. The metal is coordinated to two Cl ligands in *cis* positions and to four N atoms from the tetradentate ligand. The two N atoms from the pyrrole rings are not coordinated to the metal. The chelate angles N(1)—Cd—N(1^{i}) and N(2)—Cd—N(2^{i}) [symmetry code: (i) $-x+1$, $-y$, z] have values of 75.8 and 71.1°, respectively, and represent the most pronounced differences from regular octahedral geometry.

The cadmium–nitrogen interatomic distances, Cd—N(azomethine) 2.45 (1) Å and Cd—N(amine) 2.458 (9) Å, are almost equal in length; they do not differ very much from those found in other hexacoordinated Cd complexes with five-membered chelate rings around the metal atom, *e.g.* in (1,2-benzenediamine-*N*)[*N*,*N*″-(2,6-pyridinediyldimethylidene)bis(1,2-benzenediamine)]cadmium(II) diperchlorate, [Cd—N(azomethine) 2.377 (10) Å and Cd—N(amine) 2.426 (12) Å (Nelson, Esho & Drew, 1982)], or in (bipy)Cd(S_2CNEt_2) [2.430 (3) Å], $(phen)_2Cd(S_2CNEt_2)_2$ [2.42 (1) Å] (Arioldi, de Oliveira, Riggiero & Lechat, 1990) and in bis[(2-aminoethyl)amine]dichlorocadmium(II) [2.37 (2) Å (Cannas, Marongin & Saba, 1980)]. This latter polymeric complex, having a CdN_4Cl_2 'core' with both bridging and terminal Cl ligands and N atoms forming five-membered chelating rings in the coordination sphere, provides the closest comparison with the subject of this paper. In fact, the bond length Cd—Cl(terminal), 2.49 (1) Å, is similar to that found in our complex, 2.533 (3) Å.

Acta Crystallographica Section C
ISSN 0108-2701 © 1994