

Solvent–metal interactions in bis[1,2-dicarba-*closo*-dodecaboran(12)-1-yl]mercury(II) dichloromethane solvate and bis[1,12-dicarba-*closo*-dodecaboran(12)-1-yl]-mercury(II) tetrahydrofuran solvate

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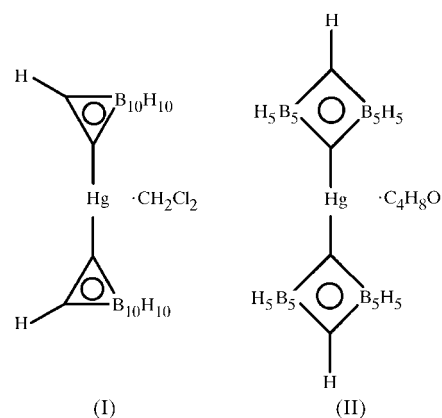
The title compounds, bis[1,2-dicarba-*closo*-dodecaboran(12)-1-yl]mercury(II) dichloromethane solvate, [Hg(C₂B₁₀H₁₁)₂]·CH₂Cl₂, (I), and bis[1,12-dicarba-*closo*-dodecaboran(12)-1-yl]mercury(II) tetrahydrofuran solvate, [Hg(C₂B₁₀H₁₁)₂]·C₄H₈O, (II), were prepared in excellent yields using a robust synthetic procedure involving the reaction of HgCl₂ with the appropriate monolithiocarborane. X-Ray analysis of the products revealed strong interactions between the Hg atoms in both complexes and the respective lattice solvent. The distances between the Hg^{II} centers and the Cl atoms of the dichloromethane solvent molecule in the *ortho*-carborane derivative, (I), and the O atom of the tetrahydrofuran molecule in the *para*-carborane complex, (II), are shorter than the sums of the van der Waals radii for Hg and Cl (3.53 Å), and Hg and O (3.13 Å), respectively, indicating moderately strong interactions. There are two crystallographically independent molecules in the asymmetric unit of both compounds, which, in each case, are related by differing relative positions of the cages.

Comment

The observation that linear mercury(II) complexes and mercuracycles interact with a variety of substrates (Beauchamp *et al.*, 1986; Wuest & Zacharie, 1987), including CO, NO and N₂ (Tevault *et al.*, 1977), has led to the development of Hg-derived molecular recognition motifs (Wuest & Zacharie, 1987) and ion-transport mediators (Zheng *et al.*, 1993). Hawthorne and co-workers have extensively investigated the

chemistry of carborane-derived tri- and tetrameric mercury macrocycles (Yang *et al.*, 1991; Zheng *et al.*, 1995; Hawthorne & Zheng, 1997), including studying their potential as catalysts (Yang *et al.*, 1991) and their ability to coordinate different anions (Zinn *et al.*, 1999).

We observed the Lewis acidic nature of simple Hg-carborane compounds during a series of experiments involving the use of RHgR complexes (*R* is *ortho*- or *para*-carborane) as reagents for the synthesis of arylcarborane derivatives (Tsvetkov *et al.*, 2000). Compounds (I) and (II) were synthesized using a modification of the procedure reported by Zakharkin *et al.* (1965), in which HgCl₂ was reacted with the corresponding monolithiated anions of *ortho*- and *para*-carborane in ether.



Crystals of (I) decompose slowly upon removal from the mother liquor and are sensitive to prolonged exposure to light. The crystal structure of (I) has two independent molecules, (IA) and (IB), in the asymmetric unit. Both molecules exhibit near-linear geometry, with the C–Hg–C angles being 175.74 (9) and 172.78 (8)°, respectively (Fig. 1). The average Hg–C bond distances are within normal ranges, with values of 2.097 (2) and 2.095 (2) Å for molecules (IA) and (IB), respectively (Wu *et al.*, 1998; Potenza & Lipscomb, 1964). All four carborane cages are slightly distorted icosahedra, with average B–B bond distances of 1.777 (4) Å in (IA) and 1.781 (4) Å in (IB), and average B–C bond distances of 1.717 (4) Å in (IA) and 1.712 (3) Å in (IB). The C atoms of each cage were identified based on the shorter C–C bond lengths of 1.671 (4) and 1.647 (3) Å for molecules (IA) and (IB), respectively. The crystal packing of (I) shows alternating layers of solvent and Hg–carborane units (Fig. 2).

Compound (II) (Fig. 3) is organized into a lattice comprised of two crystallographically independent molecules, (IIA) and (IIB), containing channels of tetrahydrofuran (THF) solvent molecules along the *b* axis. Both molecules have C–Hg–C bond angles which do not deviate significantly from linearity [173.0 (4)° in (IIA) and 177.2 (4)° in (IIB)]. The average Hg–C bond lengths for molecules (IIA) and (IIB) [2.073 (9) and 2.088 (10) Å, respectively] are slightly shorter than the same bonds in the *ortho*-carborane derivative, (I). The four carborane cages are essentially symmetrical icosahedral

polyhedra, with average B—B distances of 1.771 (18) Å in molecule (IIA) and 1.765 (18) Å in molecule (IIB), and average B—C bond lengths of 1.706 (16) and 1.700 (16) Å, respectively.

The interaction of the dichloromethane solvent molecule with Hg in (I) is surprisingly pronounced. Both independent molecules of (I) show the Cl atoms of the dichloromethane molecule closely approaching the Hg metal center, with

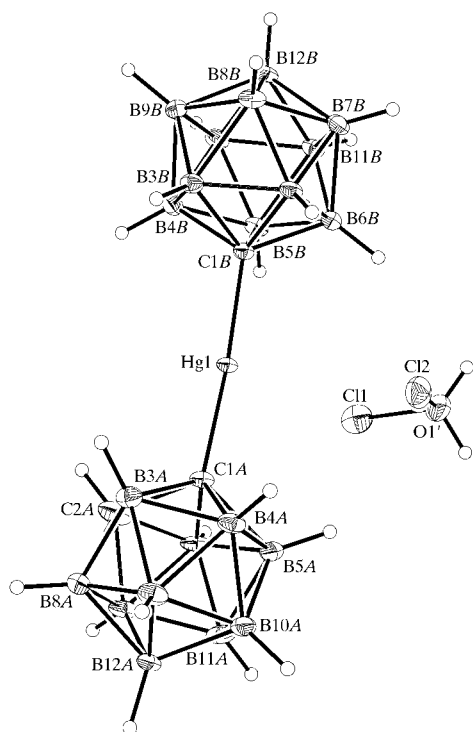


Figure 1
A view of the molecule of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii; only one of the two crystallographically independent Hg complexes and its adjacent solvent molecule is shown.

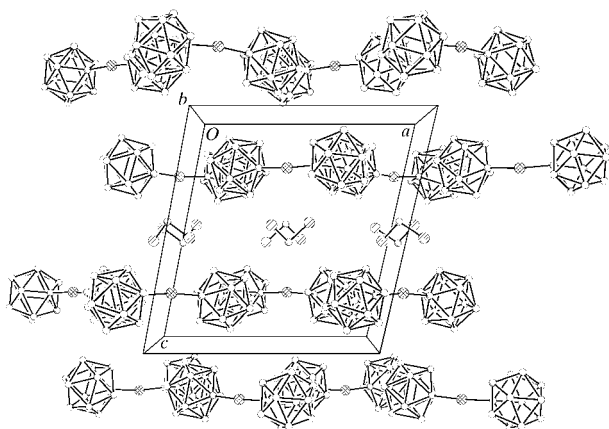


Figure 2
A packing diagram for (I), viewed along the *b* axis, showing the alternating layers of solvent and the complex.

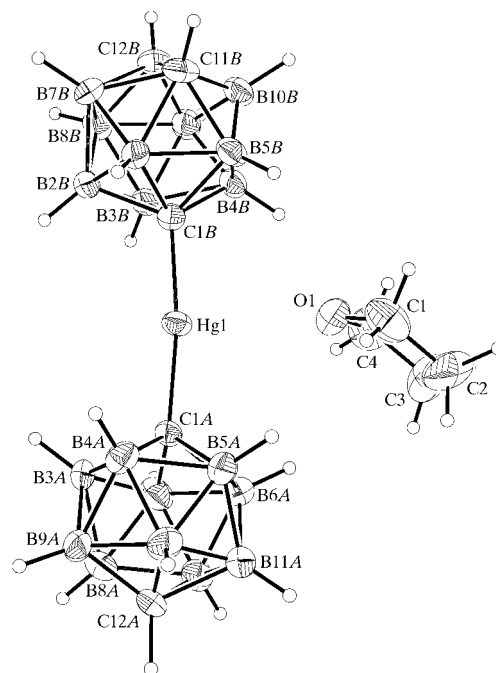


Figure 3
A view of the molecule of (II), with the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii; only one of the two crystallographically independent Hg complexes and its adjacent solvent molecule is shown.

Hg—Cl distances of 3.317 (1) and 3.389 (1) Å for molecule (IA), and 3.248 (1) and 3.252 (2) Å for molecule (IB). These distances are smaller than the van der Waals distance of 3.53 Å (Pauling, 1960) and similar to the intramolecular coordination of Cl to Hg in 1-methylmercurio-2-chloromethyl-*ortho*-carborane (Bokii *et al.*, 1978).

In compound (II), one of the two independent molecules is closely associated with the O atom of the THF solvent. The Hg—O distance of 2.850 (7) Å is again much shorter than the van der Waals sum of 3.13 Å (Pauling, 1960). Hawthorne and co-workers have reported pronounced interactions between the coordinating solvents ethanol and acetonitrile with the Hg atoms of Hg—carborane derivatives. The Hg—O(ethanol) distances in an acyclic mercury compound containing two Hg atoms and three carborane units are 2.85 (2) and 2.89 (2) Å (Zheng *et al.*, 1995), while the Hg—N(acetonitrile) distances in [9]mercuracarborand-3, having the general formula (C₂B₁₀H₁₀Hg)₃, range between 2.74 (3) and 3.13 (2) Å (Yang *et al.*, 1993).

In conclusion, this report describes the first X-ray structure determination of simple bis(carboran-1-yl)mercury(II) derivatives. The reported structures demonstrate pronounced interactions between the lattice solvent and the (Lewis) acidic Hg^{II} centers. The interaction between the Hg center and the dichloromethane Cl atoms is of particular interest, as it implies that Hg—carborane derivatives, including mercuramacrocycles, could potentially be used as recognition motifs for chloro-carbon solvents.

Experimental

The synthesis of (I) was carried out as follows: *ortho*- or *para*-carborane (1.0 g, 6.90 mmol) was dissolved in dry diethyl ether (70 ml) and cooled to 273 K. *n*-BuLi (1.6 M solution in hexanes, 6.90 mmol, 4.31 ml) was added dropwise and, after 45 min at 273 K, HgCl₂ (99.5%, 3.45 mmol, 0.941 g) was added. The resulting heterogeneous solution was warmed slowly to room temperature over a period of 45 min and then heated at reflux overnight. The reaction was quenched with water (50 ml) and the organic layer extracted with brine (50 ml). The aqueous layers were combined and further extracted with diethyl ether (3 × 20 ml). The organic layers were then combined, dried over MgSO₄ and filtered, and the solvent was removed by rotary evaporation. The resulting powder was triturated with diethyl ether, affording a white solid (1.528 g, 91%). The remaining solution was evaporated under reduced pressure, and an additional aliquot of powder was isolated by flash chromatography (CH₂Cl₂–petroleum ether, from 3:7 to 1:1; 33 mg). The solids were combined and recrystallized from a 1:1 mixture of hexanes and CH₂Cl₂, affording colorless crystals of (I) (1.562 g, 93%). Analytical data: *R*_F (1:1 CH₂Cl₂–petroleum ether) = 0.48; m.p. > 583 K. Spectroscopic data, IR (KBr, cm⁻¹): 3066 (*m*, ν_{CH}), 2592, 2572, 2502 (*s*, ν_{BH}), 1700, 1073, 1025, 722; ¹H NMR (200 MHz, CD₂Cl₂, p.p.m.): 3.90–0.90 (*m*, 20H, 2 × B₁₀H₁₀), 3.72 (*br s*, 2H, 2 × CH); ¹³C NMR (50 MHz, CD₂Cl₂, p.p.m.): 85.4 (C–Hg), 60.9 (CH); ¹¹B{¹H} NMR (160 MHz, acetone-*d*⁶, p.p.m.): –0.7, –1.9, –7.5, –10.2, –12.0; EIMS: *m/z* = 487 [*M*⁺], having the expected boron isotope distribution.

For the synthesis of (II), the same methodology was employed as used to prepare (I), except that, after the initial work-up and solvent evaporation, the resulting solid was purified by flash chromatography using petroleum ether. The product, a white solid, was crystallized from CH₂Cl₂–THF (1:1), giving (II) as colorless crystals (1.549 g, 92%). Analytical data: *R*_F (petroleum ether) = 0.70; m.p. = 531 K (decomposition). Spectroscopic data, IR (KBr, cm⁻¹): 3063 (*m*, ν_{CH}), 2615 (*s*, ν_{BH}), 1261, 1144, 1090, 1009, 823, 763, 727; ¹H NMR (200 MHz, CD₂Cl₂, p.p.m.): 3.80–0.30 (*m*, 20H, 2 × B₁₀H₁₀), 2.50 (*br s*, 2H, 2 × CH); ¹³C NMR (50 MHz, CD₂Cl₂, p.p.m.): 93.8 (C–Hg), 68.6 (CH); ¹¹B{¹H} NMR (160 MHz, acetone-*d*⁶, p.p.m.): –11.6, –12.6; EIMS: *m/z* = 488 [*M*⁺], having the expected boron isotope distribution.

Compound (I)

Crystal data

[Hg(C ₂ B ₁₀ H ₁₁) ₂] ₂ ·CH ₂ Cl ₂	<i>Z</i> = 4
<i>M</i> _r = 571.94	<i>D</i> _x = 1.753 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 12.4673 (18) Å	Cell parameters from 29 083 reflections
<i>b</i> = 13.5634 (18) Å	<i>θ</i> = 3.1–36.3°
<i>c</i> = 13.5910 (18) Å	<i>μ</i> = 7.34 mm ⁻¹
<i>α</i> = 105.642 (4)°	<i>T</i> = 100 (2) K
<i>β</i> = 101.243 (4)°	Plate, colorless
<i>γ</i> = 90.381 (5)°	0.25 × 0.20 × 0.08 mm
<i>V</i> = 2166.4 (5) Å ³	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	17 966 independent reflections
<i>φ</i> and <i>ω</i> scans	15 490 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 1997)	<i>R</i> _{int} = 0.031
<i>T</i> _{min} = 0.298, <i>T</i> _{max} = 0.556	<i>θ</i> _{max} = 36.3°
44 711 measured reflections	<i>h</i> = –16 → 20
	<i>k</i> = –22 → 19
	<i>l</i> = –21 → 22

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0186P)^2 + 0.6468P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.062$	(Δ/ <i>σ</i>) _{max} = 0.005
<i>S</i> = 1.05	Δ <i>ρ</i> _{max} = 2.18 e Å ⁻³
17 966 reflections	Δ <i>ρ</i> _{min} = –2.03 e Å ⁻³
506 parameters	Extinction correction: SHELXTL (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.00133 (8)

Compound (II)

Crystal data

[Hg(C ₂ B ₁₀ H ₁₁) ₂] ₂ ·C ₄ H ₈ O	<i>D</i> _x = 1.583 Mg m ⁻³
<i>M</i> _r = 559.11	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Cell parameters from 21 394 reflections
<i>a</i> = 12.186 (7) Å	<i>θ</i> = 3.4–27.4°
<i>b</i> = 19.548 (12) Å	<i>μ</i> = 6.56 mm ⁻¹
<i>c</i> = 19.700 (12) Å	<i>T</i> = 173 (2) K
<i>β</i> = 90.055 (10)°	Plate, colorless
<i>V</i> = 4693 (5) Å ³	0.35 × 0.30 × 0.12 mm
<i>Z</i> = 8	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	10 466 independent reflections
<i>φ</i> and <i>ω</i> scans	8750 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Bruker, 1997)	<i>R</i> _{int} = 0.050
<i>T</i> _{min} = 0.175, <i>T</i> _{max} = 0.455	<i>θ</i> _{max} = 27.5°
34 377 measured reflections	<i>h</i> = –15 → 15
	<i>k</i> = –25 → 25
	<i>l</i> = –25 → 22

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	(Δ/ <i>σ</i>) _{max} = 0.002
<i>S</i> = 1.06	Δ <i>ρ</i> _{max} = 3.05 e Å ⁻³
10 466 reflections	Δ <i>ρ</i> _{min} = –3.38 e Å ⁻³
557 parameters	Extinction correction: SHELXTL (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.00029 (4)

For both compounds, the H atoms were placed geometrically and refined using a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.2*U*_{eq}(B). C–H(carborane) and B–H(carborane) distances were constrained to 1.14 Å. Atom C4' in compound (II) was intentionally refined isotropically due to the detrimental effect that anisotropic refinement at this position had on the least-squares analysis of that model. This is most likely to be due to the disordered nature of the THF solvent molecule in the crystal lattice of (II). The crystal used to collect the data for (II) was twinned. An initial unit-cell determination gave the orthorhombic *mmm* system. However, upon integration, it was apparent that this was incorrect, as no appropriate set of systematic absences was present. A search for alternative metric symmetry revealed three potential monoclinic systems, of which one contained a more favourable *R*(*sym*). Upon re-integrating the data in the monoclinic Laue class *2/m*, followed by redetermination of the absorption correction, a unit cell was found, but solution determination was still problematic. Introduction of the (100/0–10/00–1) twin law led to an immediate benefit upon least-squares analysis and the refinement proceeded smoothly to the final reported model.

For both compounds, data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL and WinGX (Farrugia, 1999); software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1042). Services for accessing these data are described at the back of the journal.

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