

The structure was solved by the Patterson method using *SHELXS86* (Sheldrick, 1985). All H atoms, located by difference Fourier synthesis, were left riding with the distances to their parent atoms constrained; a global isotropic displacement parameter was refined. The full-matrix least-squares refinements were carried out using *SHELX76* (Sheldrick, 1976). Molecular graphics were produced using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: PA1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cs[CB₁₀H₁₃] at 293 K

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Abstract

The unit cell of the room-temperature phase of Cs[CB₁₀H₁₃], caesium 8,9:10,11-di- μ -hydro-undeca-hydro-7-carba-*nido*-undecaborate(1⁻), is found to be very similar to that of γ -Cs[C₂B₉H₁₂] at 299 K reported previously [Rius, Romerosa, Teixidor, Casabó & Miravittles (1991). *Inorg. Chem.* **30**, 1376–1379], but the packing of the carborane anion cages around the Cs⁺ ions is distorted further from ideal octahedral geometry and the uncapped pentagonal faces of the cages lie

parallel to the *a* axis. No evidence of increased conductivity in two higher-temperature phases has been found for this compound.

Comment

A study of three polymorphs of Cs[C₂B₉H₁₂] in the temperature range 293–323 K has been reported previously (Rius, Romerosa, Teixidor, Casabó & Miravittles, 1991). The structure at 299 K has been described as a distorted hexagonal close-packed arrangement of anions with Cs⁺ cations at the octahedrally coordinated sites. With increasing temperature, a transition to a conducting phase occurred between 471.8 and 495 K, associated with a change in the anion packing arrangement about Cs⁺ from distorted octahedral (γ , β phases) to tetrahedral (α phase, conducting) and disorder of the Cs⁺ ions along the *c* axis of the tetragonal cell. The structure of Cs[CB₁₀H₁₃], (I), at 293 K was determined in order to investigate the effects of slight changes in the electronic configuration, symmetry and H-atom geometry of the carborane anion on the structure and conductivity of the carborano caesium salts, while keeping the overall charge and carborane cage geometry constant.

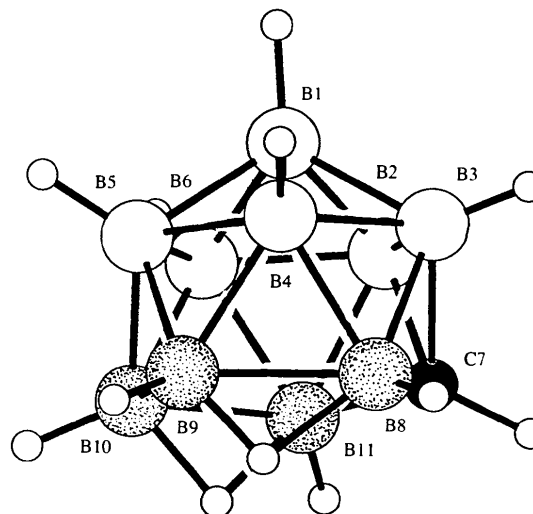
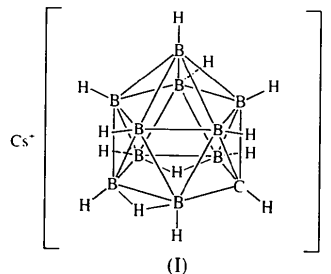


Fig. 1. A *PLUTO* (Motherwell & Clegg, 1978) plot of the [CB₁₀H₁₃]⁻ anion with the atomic numbering scheme. This anion displays internal mirror symmetry, in contrast to [C₂B₉H₁₂]⁻, which has only one bridging H atom on the pentagonal ring.

The structure of the $[\text{CB}_{10}\text{H}_{13}]^-$ anion is shown in Fig. 1. The cell parameters of $\text{Cs}[\text{CB}_{10}\text{C}_{13}]$ at 293 K [monoclinic, $P2_1/a$, $a = 12.162(1)$, $b = 10.647(1)$, $c = 7.985(1)$ Å, $\beta = 92.441(5)^\circ$] are intermediate between those of γ - and β - $\text{Cs}[\text{C}_2\text{B}_9\text{H}_{12}]$. The unit-cell parameters and positional parameters for the Cs^+ ions and geometric centres of the carborane cages for the three structures with respect to the $P2_1/a$ cell are given in Table 1. Fig. 2 shows that the octahedral packing geometry around the Cs^+ ions in $\text{Cs}[\text{CB}_{10}\text{H}_{13}]$ is more distorted from the ideal than in γ - $\text{Cs}[\text{C}_2\text{B}_9\text{H}_{12}]$. Average bond lengths for the carborane cage and $\text{Cs}\cdots\text{B}$ contact distances for $\text{Cs}[\text{CB}_{10}\text{H}_{13}]$ are given in Table 2. The principal difference in the two structures is the alignment of the uncapped pentagonal faces of the

carborane cages with respect to the channels of the Cs^+ ions and the pseudo-hexagonal axis in $\text{Cs}[\text{CB}_{10}\text{H}_{13}]$, shown in Fig. 2. In γ - $\text{Cs}[\text{C}_2\text{B}_9\text{H}_{12}]$ the uncapped pentagonal faces of the cages are tilted with respect to these channels and all three cell axes. The orientation of the uncapped cage faces could not be determined from the powder diffraction data for β - $\text{Cs}[\text{C}_2\text{B}_9\text{H}_{12}]$.

An investigation of the two higher-temperature phases of $\text{Cs}[\text{CB}_{10}\text{H}_{13}]$ has revealed no substantial increase in conductivity with increase in temperature (Romerosa, 1992). Indexing the powder diffraction data for these phases has not yet proved possible, as substantial and systematic overlap of reflections results from the pseudo-sphericity of the carborane anions (Rius, unpublished results).

These results indicate that slight changes in the electronic configuration or H-atom geometry of the carborane anion modify the conductivity of the carborane caesium salts to a significant extent, and that the orientation of the pentagonal faces of the anion with respect to the cations may be an important factor in determining the solid-state behaviour of the salts.

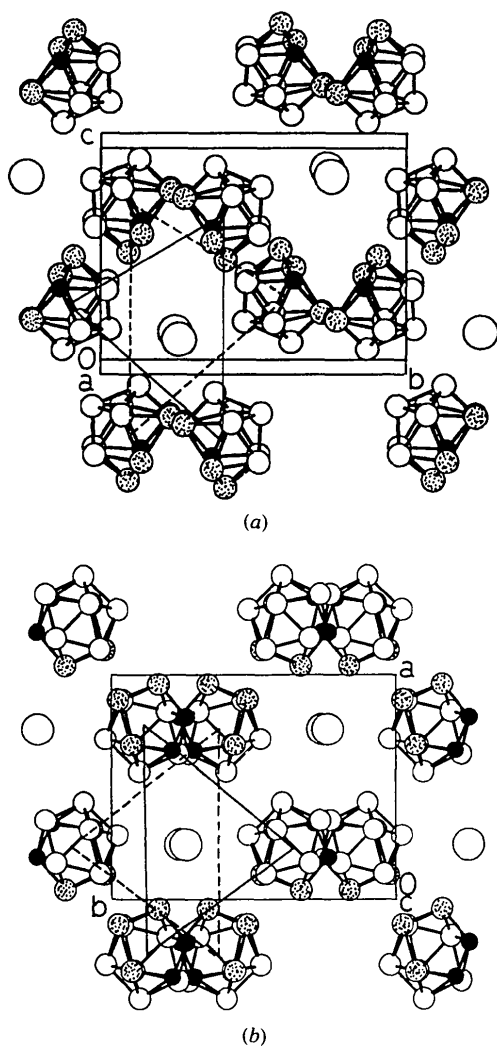


Fig. 2. PLUTO (Motherwell & Clegg, 1978) plots of the unit cells for (a) $\text{Cs}[\text{CB}_{10}\text{H}_{13}]$ and (b) γ - $\text{Cs}[\text{C}_2\text{B}_9\text{H}_{12}]$ (Rius, Romerosa, Teixidor, Casabó & Miravittles, 1991) showing upper and lower triangular faces of the distorted octahedral caesium environments. Atoms are shaded in accordance with Fig. 1.

Experimental

The title compound was prepared according to the method of Knoth (1971).

Crystal data

$\text{Cs}[\text{CB}_{10}\text{H}_{13}]$
 $M_r = 266.11$
 Monoclinic
 $P2_1/a$
 $a = 12.162(1)$ Å
 $b = 10.647(1)$ Å
 $c = 7.985(1)$ Å
 $\beta = 92.441(5)^\circ$
 $V = 1033.1(3)$ Å³
 $Z = 4$
 $D_x = 1.71$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 11.96$ – 20.70°
 $\mu = 3.47$ mm⁻¹
 $T = 293$ K
 Rectangular block
 $0.37 \times 0.35 \times 0.2$ mm
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: empirical (ψ scan)
 $T_{\min} = 0.513$, $T_{\max} = 1.000$
 2188 measured reflections
 1978 independent reflections

1879 observed reflections
 $[I \geq 2.5\sigma(I)]$
 $R_{\text{int}} = 0.011$
 $\theta_{\max} = 26.2^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 13$
 $l = -9 \rightarrow 9$
 3 standard reflections
 frequency: 60 min
 intensity decay: -4.7%

Refinement

Refinement on F
 $R = 0.042$
 $wR = 0.051$
 $S = 2.47$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.447$ e Å⁻³
 $\Delta\rho_{\min} = -0.911$ e Å⁻³
 Extinction correction: none

1879 reflections Atomic scattering factors
142 parameters from *International Tables*
 $w = 9.3387/[\sigma^2(F)$ for *X-ray Crystallography*
 $+ 0.000176(F)^2]$ (1974, Vol. IV)

Table 1. *The unit-cell parameters, Cs⁺ ion position and centre of the anion in Cs[CB₁₀H₁₃] and β- and γ-Cs[C₂B₉H₁₂] referred to a unit cell with P2₁/a setting*

Cell parameters (Å, °)	γ-Cs[C ₂ B ₉ H ₁₂] ^a	Cs[CB ₁₀ H ₁₃] ^b	β-Cs[C ₂ B ₉ H ₁₂] ^c
<i>a</i>	11.222 (4)	12.162 (1)	12.15 (2)
<i>b</i>	10.696 (4)	10.647 (1)	12.55 (2)
<i>c</i>	8.360 (3)	7.985 (1)	6.90 (2)
β	92.62 (2)	92.441 (5)	90.0 (1)
Cs ⁺ position			
<i>x</i>	0.5106 (1)	0.51065 (3)	0.508 (8)
<i>y</i>	0.2591 (1)	0.24381 (3)	0.241 (6)
<i>z</i>	0.2428 (1)	0.15785 (4)	0.111 (3)
Geometric centre of anion			
<i>x</i>	0.2482	0.2427 (5)	0.28
<i>y</i>	0.1231	0.0916 (5)	0.061
<i>z</i>	0.7692	0.7063 (7)	0.65

References: (a) Rius, Romerosa, Teixidor, Casabó & Miravittles (1991); (b) this work.

Table 2. *Average carborane-cage bond lengths and Cs⁺⋯B contact distances (Å)*

B—B _{average}	1.785 (8)	B9⋯Cs ⁱⁱⁱ	3.752 (6)
B—C _{average}	1.66 (1)	B3⋯Cs ^{iv}	3.767 (6)
B5⋯Cs ⁱ	3.695 (5)	B11⋯Cs ^v	4.014 (6)
B2⋯Cs ⁱⁱ	3.728 (5)	B10⋯Cs	4.083 (6)

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

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for Cs[CB₁₀H₁₃]*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cs	0.51065 (3)	0.24381 (3)	0.15785 (4)	0.0414 (3)
B1	0.2495 (4)	-0.0280 (5)	0.8123 (7)	0.032 (3)
B2	0.1615 (4)	-0.0199 (5)	0.6295 (7)	0.035 (3)
B3	0.1323 (4)	0.0688 (5)	0.8111 (8)	0.034 (3)
B4	0.2555 (5)	0.1254 (5)	0.9028 (7)	0.031 (3)
B5	0.3630 (4)	0.0692 (5)	0.7798 (7)	0.032 (3)
B6	0.3043 (5)	-0.0197 (5)	0.6061 (7)	0.033 (3)
C7	0.1246 (4)	0.1338 (5)	0.6194 (7)	0.036 (3)
B8	0.1745 (5)	0.2254 (6)	0.7683 (8)	0.031 (3)
B9	0.3267 (5)	0.2286 (5)	0.7691 (8)	0.033 (3)
B10	0.3582 (5)	0.1342 (6)	0.5796 (8)	0.038 (3)
B11	0.2195 (5)	0.0899 (6)	0.4917 (7)	0.041 (3)

The H atoms were located from difference Fourier maps. The positions of the 11 non-bridging H atoms were refined and the positions of the two bridging H atoms were fixed with $U_{iso} = 1.25 \times U_{eq}(C, B_{parent})$ for all H atoms.

Data collection and cell refinement: *CAD-4 Express Operating Software* (Enraf-Nonius, 1992). Data reduction: *MolEN* (Fair, 1990). Structure solution: *MULTAN11/84* (Main, Germain & Woolfson, 1984). Structure refinement: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(hexadecylpyridinium) Bis(3,6-dichloro-4,5-dihydroxy-3,5-cyclohexadiene-1,2-dionato-κ²O⁴,O⁵)beryllium

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Abstract

The title compound, 2C₂₁H₃₈N[Be(C₆Cl₂O₄)₂]₂, contains complex anions formed by two 3,6-dichloro-4,5-dihydroxy-3,5-cyclohexadiene-1,2-dionato residues, tetrahedrally coordinating to beryllium through deprotonated hydroxy O atoms, and hexadecylpyridinium