

Structure of Caesium 3,3'-*commo*-Bis(decahydro-8-iodo-1,2-dicarba-3-cobalta-*closo*-dodecaborate)(1-)

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Abstract. Cs[Co(C₂H₁₀B₉I)₂], $M_r = 708.4$, monoclinic, $P2_1/n$, $a = 6.813$ (1), $b = 14.656$ (1), $c = 10.637$ (1) Å, $\beta = 101.45$ (1)°, $V = 1041.0$ Å³, $Z = 2$, $D_m = 2.24$, $D_x = 2.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.44$ mm⁻¹, $F(000) = 644$, $T = 293$ K. Final $R = 0.025$ for 1856 observed reflections. A double-cage anion with Co at a centre of symmetry creates a symmetric π -sandwich complex. The Cs⁺ cation is situated at another, crystallographically independent, centre of symmetry. The B(8)–I bond distance is 2.205 (5) Å. It is shown that ligand pseudosymmetry has no effect on the slip distortion of carbametallaboranes.

Introduction. The synthesis of the title compound has been described (Mátel, Macáček, Rajec, Heřmánek & Plešek, 1982). Previously we have investigated caesium salts of this type from the aspect of slip distortion (Sivý, Preisinger, Baumgartner, Valach, Koreň & Mátel, 1986) as defined by Wing (1968). In this paper we deal with the effect of ligand pseudosymmetry on the slip distortion of two-cage carbametallaboranes.

Experimental. Sample recrystallized from a solution of acetone and distilled water by slow evaporation at laboratory temperature, D_m by flotation in CHBr₃/CCl₄, prismatic crystal with dimensions 0.12 × 0.12 × 0.22 mm; Philips PW 1100 diffractometer, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\text{max}} = 55^\circ$, scan speed 0.033° s⁻¹; 17 reflections with $4.79 < 2\theta < 12.94^\circ$ used for refinement of lattice constants; absorption corrections applied, maximum and minimum transmission factors: 0.5953, 0.5036; index range $-8 \leq h \leq 8$,

$0 \leq k \leq 19$, $0 \leq l \leq 13$; three standard reflections, variation 3.0%; 2618 reflections measured, 2393 unique, $R_{\text{int}} = 0.019$, 1856 with $I \geq 3\sigma(I)$ used for structure analysis; coordinates of I and Cs obtained from Patterson map; Co and other non-H atoms located from Fourier syntheses; heavy atoms refined by full-matrix least squares using F values anisotropically, C and B isotropically; unit weights; C atoms selected as two neighbouring atoms with the lowest values of thermal coefficients ($U = 0.015\text{--}0.019$ Å²). A weighted difference Fourier synthesis [$w = 1/[\sigma^2(F_o) + 0.001476 F_o^2]$] provided positions of H atoms [except H(2) (calculated)], refined isotropically. Maximum positive and maximum negative electron densities in final difference map 0.8 and -0.7 e Å⁻³. Final $R = 0.025$, $wR = 0.031$. $(\Delta/\sigma)_{\text{max}}$ in final refinement cycle 0.055 (H atom); scattering factors and f' , f'' (for heavy atoms) from *International Tables for X-ray Crystallography* (1962). Calculations performed with XRAY72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) using an M4030-1 computer, Slovak Technical University, Bratislava, Czechoslovakia.

Discussion. The atom coordinates are shown in Table 1.* Bond distances and selected bond angles around Co and I, and average values of other types of angles are

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42462 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

listed in Table 2; the atomic numbering is shown in Fig. 1. A view of the structure of the unit cell is shown in Fig. 2.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cs	0.5	0.5	0	0.0617 (2)
I	1.0730 (1)	0.5772 (1)	0.1767 (1)	0.0403 (1)
Co	1.0	0.5	0.5	0.0190 (2)
C(1)	1.0836 (5)	0.3677 (2)	0.5318 (4)	0.023 (1)
C(2)	0.8431 (6)	0.3816 (3)	0.4833 (4)	0.026 (1)
B(4)	1.2160 (6)	0.4198 (3)	0.4316 (4)	0.026 (1)
B(5)	1.1817 (7)	0.2991 (3)	0.4316 (5)	0.030 (1)
B(6)	0.9461 (8)	0.2757 (3)	0.4688 (5)	0.034 (1)
B(7)	0.7900 (7)	0.4434 (3)	0.3470 (4)	0.027 (1)
B(8)	1.0280 (6)	0.4658 (3)	0.3074 (4)	0.025 (1)
B(9)	1.1422 (7)	0.3592 (3)	0.2845 (5)	0.029 (1)
B(10)	0.9750 (7)	0.2702 (3)	0.3081 (5)	0.033 (1)
B(11)	0.7588 (7)	0.3227 (3)	0.3470 (5)	0.034 (2)
B(12)	0.8783 (7)	0.3731 (3)	0.2322 (4)	0.028 (1)

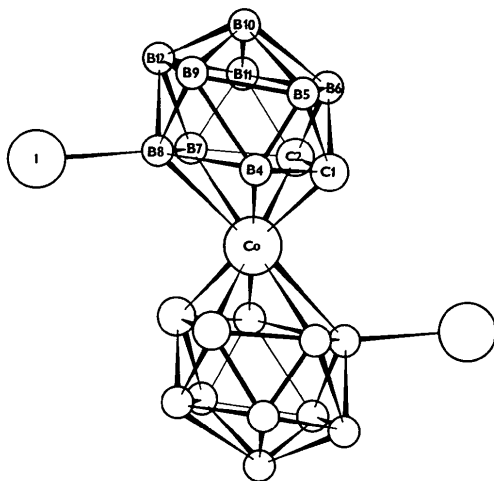


Fig. 1. The $[(C_2B_9H_{10}I)_2Co]^-$ anion with atom labelling (H atoms omitted).

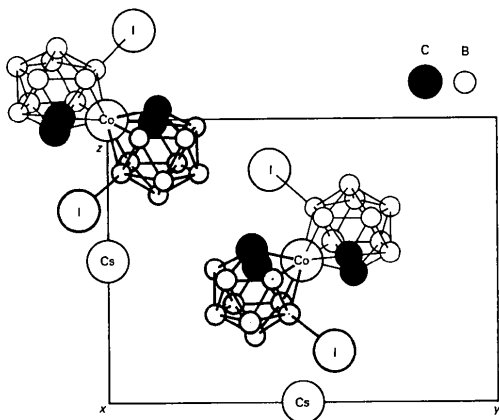


Fig. 2. Projection of the structure on (100).

The Cs^+ cation is 'ion-bonded' to the complex $[(C_2B_9H_{10}I)_2Co]^-$ anion. The nearest atoms to Cs^+ are H(12) 2.95 (8) \AA and B(12) 3.697 (10) \AA . The closest intermolecular contacts of each principal type are $I \cdots H = 2.85$ (5), $C \cdots H = 3.06$ (5), $B \cdots H = 2.74$ (5), and $H \cdots H = 2.53$ (7) \AA .

Table 2. Bond distances (\AA) and selected angles ($^\circ$) with e.s.d.'s in parentheses

Co—C(1)	2.030 (3)	B(5)—B(6)	1.761 (8)
—C(2)	2.027 (4)	—B(9)	1.769 (8)
—B(4)	2.122 (7)	B(6)—B(11)	1.768 (11)
—B(7)	2.112 (12)	B(7)—B(8)	1.785 (8)
—B(8)	2.154 (5)	—B(11)	1.782 (6)
C(1)—C(2)	1.630 (7)	—B(12)	1.791 (8)
—B(4)	1.707 (8)	B(8)—B(9)	1.783 (6)
—B(5)	1.696 (8)	—B(12)	1.789 (8)
—B(6)	1.702 (7)	B(9)—B(12)	1.785 (9)
C(2)—B(6)	1.723 (6)	B(10)—B(5)	1.776 (12)
—B(7)	1.687 (7)	—B(6)	1.761 (8)
—B(11)	1.687 (8)	—B(9)	1.782 (7)
B(4)—B(5)	1.784 (6)	—B(11)	1.782 (8)
—B(8)	1.780 (11)	—B(12)	1.775 (7)
—B(9)	1.783 (8)	B(11)—B(12)	1.759 (9)
C(1)—H(1)	0.93 (4)	Average bond lengths within the	
C(2)—H(2)	1.02 (6)	$[(C_2B_9H_{10}I)_2Co]^-$ anion	
B(4)—H(4)	1.09 (5)	Bond type	No.
B(5)—H(5)	1.10 (4)	Co—C	2
B(6)—H(6)	0.95 (4)	Co—B	3
B(7)—H(7)	1.10 (4)	C—C	1
B(9)—H(9)	1.11 (5)	C—B	6
B(10)—H(10)	1.17 (7)	B—B	18
B(11)—H(11)	1.13 (5)	C—H	2
B(12)—H(12)	1.06 (4)	B—H	8
			40
C(1)—Co—C(2)	47.4 (1)	B(4)—Co—B(7)	85.9 (2)
—B(4)	48.5 (2)	—B(8)	49.2 (2)
—B(7)	83.0 (2)	B(7)—Co—B(8)	49.5 (2)
—B(8)	82.0 (2)	I—B(8)—Co	118.5 (2)
C(2)—Co—B(4)	83.4 (2)	—B(4)	125.4 (3)
—B(7)	48.0 (2)	—B(7)	122.1 (2)
—B(8)	82.1 (2)	—B(9)	116.3 (3)
		—B(12)	114.8 (2)
			60
			60

Average bond angles around all triangular faces

Angle type	No.	Av. ^a
C—Co—C	1	47.4 (1) ^b
C—Co—B	2	48.3 (0.3)
B—Co—B	2	49.3 (0.2)
Co—C—C	2	66.3 (0.1)
Co—C—B	2	68.6 (0.1)
Co—B—C	2	63.2 (0.3)
Co—B—B	4	65.3 (1.3)
C—C—B	2	61.6 (0.9)
C—B—C	1	56.8 (2) ^b
B—C—B	4	63.0 (0.6)
C—B—B	8	58.5 (0.7)
B—B—B	30	60.0 (0.4)

Average bond angles around all pentagonal rings

Angle type	No.	Av. ^a
C—Co—B	4	82.6 (0.7)
B—Co—B	1	85.9 (2) ^b
Co—C—B	4	125.6 (1.1)
Co—B—B	6	117.6 (1.0)
C—C—B	4	111.5 (0.4)
B—C—B	2	115.3 (0.1)
C—B—B	12	104.4 (0.6)
B—B—B	27	108.0 (0.5)

(a) E.s.d.'s for averaged bond lengths and angles calculated from the equation $\delta = [\sum_{i=1}^n (x_i - \bar{x})^2 / (n-1)]^{1/2}$, where x_i is the i th value and \bar{x} is the mean of the n values. (b) Estimated standard deviation.

The slip-distortion value (Wing, 1968), the distance between the centroid of the least-squares plane defined by atoms C(1), C(2), B(4), B(7), and B(8) (Fig. 1) and the projection of the Co atom onto this plane, is 0.061 (2) Å. The title compound thus belongs to the class of symmetric π -sandwich complexes.

Two-cage carbametallaboranes, not combined with a bond, with two neighbouring C atoms in each cage directly bonded to the metal were investigated with respect to the ligand pseudosymmetry. Let d be the distance between the atom in the structure and its projection onto the selected plane, and $\sigma(d)$ the corresponding estimated standard deviation. The two atoms on the opposite sides of this plane are mirror images (on statistical significance level of 0.05) if $||d_1| - |d_2|| \leq 1.96\sqrt{\sigma^2(d_1) + \sigma^2(d_2)}$. The chosen least-squares plane is defined by the atoms Co, B(8), B(6), and B(10) (Fig. 1). If for all four pairs of atoms [B(4), B(7); B(5), B(11); B(9), B(12); C(1), C(2)] the corresponding distances satisfy this condition, the

selected plane can be considered a mirror plane m (C_s) of the icosahedron. Carrying out this test for ligand pseudosymmetry on the two-cage carbametallaboranes listed by Sivý *et al.* (1986) shows that there is no correlation between the results of the test and the magnitudes of the slip distortion.

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Structure of Caesium 8-Iodo-3,3'-*commo*-bis(decahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborate)(1-)*

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Abstract. Cs[Co(C₂H₁₁B₉)(C₂H₁₀B₉I)], $M_r = 582.53$, monoclinic, $P2_1/n$, $a = 20.721$ (4), $b = 13.167$ (1), $c = 7.462$ (1) Å, $\beta = 95.00$ (1)°, $V = 2028.1$ Å³, $Z = 4$, $D_m = 1.91$, $D_x = 1.91$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) =$

0.71069 Å, $\mu = 3.89$ mm⁻¹, $F(000) = 1080$, $T = 293$ K. Final $R = 0.045$ for 2579 observed reflections. The molecule of *closo*-carbacobaltaborane consists of two icosahedra around the Co atom, creating a π -sandwich conformation. The two neighbouring C atoms of the icosahedral fragments were distinguished unambiguously from the B atoms. In the structure there are two enantiomorphic rotational isomers.

* Alternative name: caesium (η -undecahydrido-7,8-dicarba-*nido*-undecaborato)(η -decahydrido-10-iodo-7,8-dicarba-*nido*-undecaborato)cobaltate(1-).