

## Crystal and Molecular Structure of the Bimetallocarborane Complex: Tetramethylammonium 2,3-Di- $\eta$ -cyclopentadienyl-2,3-dicobalta-1-carbadodecaborate

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$[\text{N}(\text{CH}_3)_4]^+[(\eta\text{-C}_5\text{H}_5)_2\text{Co}_2\text{CB}_9\text{H}_{10}]^-$  is monoclinic, space group  $P2_1/n$ , with  $a = 9.974$  (9),  $b = 12.909$  (9),  $c = 16.181$  (13) Å,  $\gamma = 97.466$  (62)°,  $Z = 4$ . The structure was refined to  $R = 0.038$  for 2085 counter reflexions. The anion can be described as an icosahedron with two Co, one C and nine B atoms at its vertices. Each Co atom is coordinated to one cyclopentadienyl ring.

### Introduction

The present study reports the results of the X-ray investigation of a tetramethylammonium salt of a new bimetallocarborate complex with one C atom in the carborane polyhedron. Crystals were prepared in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences in Řež near Praha (Dolanský, Baše & Štíbr, 1977).

### Experimental

The fragile black crystals are stable in air and do not decompose on exposure to X-rays. The monoclinic space group  $P2_1/n$  and preliminary lattice constants were determined from photographs (Cu  $K\alpha$  radiation). Refined cell parameters were obtained by least-squares calculations from 20 reflexions centred on the diffractometer. The crystal data are summarized in Table 1.

A crystal  $0.4 \times 0.1 \times 0.1$  mm was used for data collection. The intensities were collected on a four-circle automatic Syntex  $P2_1$  diffractometer with Mo  $K\alpha$  radiation (graphite monochromator) and the  $\omega/2\theta$  scan technique. The scan speed varied from 0.95 to 29.3°  $\text{min}^{-1}$  and was determined from a rapid preliminary exposure. The scans were taken over the range  $2\theta(K\alpha_1) - 1.0^\circ$  to  $2\theta(K\alpha_2) + 1.0^\circ$ . 2085 independent reflexions

were measured to the limit  $2\theta = 41^\circ$ . 347 of these were considered to be unobserved according to the criterion  $I < 1.96\sigma(I)$  where  $I = [\text{TC} - (B_1 + B_2)]R$  and  $\sigma(I) = [(\text{TC} + B_1 + B_2)R^2 + (0.015I)^2]^{1/2}$  (TC = total count,  $R$  = rate of the scan,  $B_1$  and  $B_2$  = background counts measured at each end of the scan for 0.5 of the scan time). All unobserved reflexions were used during the refinement. The intensities of three standards measured after every 50 reflexions showed no significant variations. The intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction.

### Structure determination and refinement

The structure was solved by the heavy-atom method. The coordinates of the two Co atoms were determined from a sharpened Patterson map. Electron density synthesis based on these input parameters provided the positions of all remaining non-hydrogen atoms.

The polyhedral C atom was distinguished from B by its higher electron density, lower temperature factor and shorter bond distances.

Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974).

The scale and overall temperature factors estimated from a Wilson plot were used for full-matrix least-squares refinement of the positional parameters. A refinement was then carried out with isotropic temperature factors ( $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.088$ ) and later with anisotropic factors for all non-hydrogen atoms ( $R = 0.061$ ). The function minimized was  $w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma(F)$  [derived from  $\sigma(I)$ ]. A subsequent difference synthesis revealed the positions of 20 H atoms. Ten of them are terminal H

Table 1. *Crystal data*

$[\text{N}(\text{CH}_3)_4]^+[(\text{C}_5\text{H}_5)_2\text{Co}_2\text{CB}_9\text{H}_{10}]^-$	Monoclinic, $P2_1/n$
$a = 9.974$ (9) Å	$Z = 4$
$b = 12.909$ (9)	$M_r = 441.74$
$c = 16.181$ (13)	$D_m = 1.423$ $\text{g cm}^{-3}$
$\gamma = 97.466$ (62)°	$D_c = 1.419$
$V = 2065.70$ (27) Å <sup>3</sup>	$\lambda(\text{Mo } K\alpha) = 0.7107$ Å

bonded to B atoms and to the C atom in the polyhedron and the remaining ten are bonded to the C atoms of the cyclopentadienyl rings. Refinement including positional parameters of these H atoms reduced  $R$  to 0.048. Temperature factors assigned to the H atoms were the same as those of the atoms to which they are bonded. A further difference synthesis located the 12 remaining H atoms of the  $[\text{N}(\text{CH}_3)_4]^+$  ion but some of these atoms did not refine well. The final cycle reduced  $R$  to 0.038. The highest residual electron density in the final difference synthesis was in the region of  $[\text{N}(\text{CH}_3)_4]^+$  and was  $0.48 \text{ e } \text{Å}^{-3}$ .

The final coordinates of the non-hydrogen atoms are given in Table 2, those of the H atoms in Table 3. The calculations were carried out on TESLA 200 and IBM 370/135 computers.

### Results and discussion

The structure is built up of  $[(\text{C}_5\text{H}_5)_2\text{Co}_2\text{CB}_9\text{H}_{10}]^-$  and  $[\text{N}(\text{CH}_3)_4]^+$  ions. Fig. 1 shows a projection of the anion

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32836 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Fractional coordinates* ( $\times 10^4$ ; for Co atoms  $\times 10^5$ ) *for the non-hydrogen atoms*

Estimated standard deviations (in parentheses) refer to the last decimal place.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	2973 (6)	3639 (4)	2730 (3)
Co(2)	17243 (7)	39621 (5)	17624 (4)
Co(3)	36357 (7)	29781 (6)	16589 (4)
B(4)	3538 (7)	2435 (5)	2852 (4)
B(5)	2366 (7)	2879 (5)	3542 (4)
B(6)	1288 (6)	3609 (6)	2984 (4)
B(7)	1541 (6)	2305 (5)	1507 (4)
B(8)	2638 (6)	1573 (5)	2114 (4)
B(9)	2128 (7)	1572 (5)	3165 (4)
B(10)	724 (7)	2291 (6)	3252 (5)
B(11)	342 (7)	2749 (5)	2238 (4)
B(12)	890 (7)	1508 (6)	2354 (4)
C(1P)	1445 (8)	4553 (5)	598 (4)
C(2P)	2490 (7)	5208 (5)	994 (4)
C(3P)	1985 (6)	5597 (4)	1718 (4)
C(4P)	597 (7)	5200 (4)	1757 (4)
C(5P)	271 (7)	4553 (5)	1066 (4)
C(6P)	4371 (5)	3442 (5)	493 (3)
C(7P)	4440 (5)	2394 (4)	627 (3)
C(8P)	5312 (6)	2335 (6)	1318 (4)
C(9P)	5723 (6)	3376 (7)	1580 (4)
C(10P)	5142 (6)	4047 (5)	1077 (4)
N	1978 (4)	8725 (3)	333 (3)
C(1T)	897 (8)	9191 (6)	763 (5)
C(2T)	3272 (11)	8952 (12)	747 (9)
C(3T)	1624 (10)	7632 (5)	159 (6)
C(4T)	2101 (11)	9218 (8)	9489 (6)

with the atomic numbering system (Adams, 1972).

The structure of the anion can be described as an icosahedron whose vertices are occupied by two Co, one C and nine B atoms. All important interatomic

Table 3. *Fractional coordinates for the hydrogen atoms*

All values are  $\times 10^3$ . Estimated standard deviations (in parentheses) refer to the last decimal place.

	<i>x</i>	<i>y</i>	<i>z</i>
H(C1)	361 (6)	428 (5)	288 (4)
H(B4)	460 (6)	245 (4)	313 (3)
H(B5)	274 (6)	312 (5)	417 (4)
H(B6)	105 (6)	429 (5)	331 (3)
H(B7)	129 (6)	204 (4)	88 (4)
H(B8)	300 (5)	88 (5)	190 (3)
H(B9)	229 (6)	89 (5)	358 (4)
H(B10)	994 (6)	210 (5)	376 (4)
H(B11)	928 (6)	278 (4)	211 (3)
H(B12)	24 (6)	79 (5)	223 (4)
H(C1P)	152 (7)	418 (5)	14 (4)
H(C2P)	349 (6)	537 (4)	88 (4)
H(C3P)	252 (6)	596 (4)	215 (4)
H(C4P)	995 (6)	525 (4)	226 (4)
H(C5P)	935 (7)	419 (5)	102 (4)
H(C6P)	386 (5)	366 (5)	8 (3)
H(C7P)	399 (5)	181 (4)	38 (3)
H(C8P)	549 (7)	184 (6)	151 (4)
H(C9P)	624 (6)	349 (6)	196 (4)
H(C10P)	530 (6)	482 (5)	114 (4)
H(1C1T)	83 (8)	877 (7)	126 (5)
H(2C1T)	3 (7)	897 (6)	47 (5)
H(3C1T)	132 (8)	1 (6)	88 (5)
H(1C2T)	339 (8)	977 (9)	76 (7)
H(2C2T)	362 (10)	844 (10)	57 (8)
H(3C2T)	248 (9)	847 (9)	126 (8)
H(1C3T)	119 (8)	721 (5)	45 (5)
H(2C3T)	252 (9)	745 (5)	988 (5)
H(3C3T)	78 (8)	746 (5)	971 (5)
H(1C4T)	254 (9)	4 (7)	945 (5)
H(2C4T)	264 (9)	866 (6)	915 (5)
H(3C4T)	110 (10)	923 (7)	930 (5)

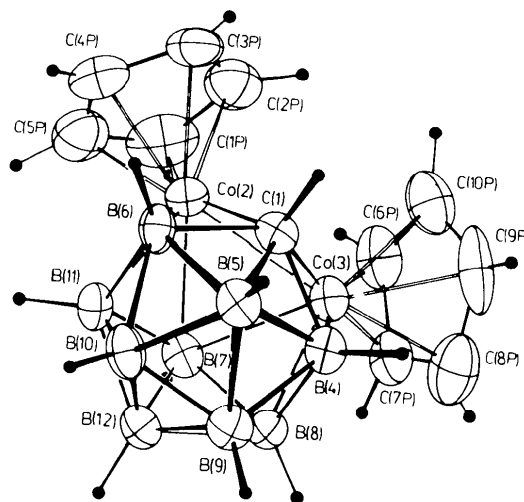


Fig. 1. Structure and numbering of the  $[(\text{C}_5\text{H}_5)_2\text{Co}_2\text{CB}_9\text{H}_{10}]^-$  anion. The hydrogen atoms have been given an arbitrary radius of 0.075 Å.

Table 4. *Interatomic distances (Å) and angles (°)*

Estimated standard deviations (in parentheses) refer to the last decimal place.

(I) Distances of non-hydrogen atoms in the icosahedral cage, arranged to show its  $C_5$  symmetry

Co(2)–Co(3)	2.430 (2)	Co(3)–C(1)	2.077 (5)
Co(2)–C(1)	2.077 (6)	Co(3)–B(4)	2.051 (6)
Co(2)–B(6)	2.063 (7)	Co(3)–B(7)	2.170 (7)
Co(2)–B(7)	2.163 (7)	Co(3)–B(8)	2.086 (6)
Co(2)–B(11)	2.093 (7)		
C(1)–B(5)	1.702 (9)	C(1)–B(4)	1.731 (9)
C(1)–B(6)	1.726 (9)		
B(5)–B(6)	1.766 (11)	B(4)–B(5)	1.765 (11)
B(5)–B(10)	1.776 (10)	B(5)–B(9)	1.781 (10)
B(6)–B(10)	1.775 (10)	B(4)–B(9)	1.752 (9)
B(6)–B(11)	1.819 (10)	B(4)–B(8)	1.791 (10)
B(7)–B(11)	1.827 (10)	B(7)–B(8)	1.823 (10)
B(7)–B(12)	1.786 (10)		
B(9)–B(10)	1.783 (11)	B(8)–B(9)	1.774 (11)
B(10)–B(11)	1.801 (11)	B(9)–B(12)	1.796 (11)
B(10)–B(12)	1.789 (11)	B(8)–B(12)	1.778 (10)
B(11)–B(12)	1.769 (11)		

(II) Cobalt–cyclopentadienyl distances

Co(2)–C(1P)	2.064 (6)	Co(3)–C(6P)	2.084 (6)
Co(2)–C(2P)	2.097 (7)	Co(3)–C(7P)	2.039 (6)
Co(2)–C(3P)	2.094 (5)	Co(3)–C(8P)	2.037 (7)
Co(2)–C(4P)	2.070 (6)	Co(3)–C(9P)	2.083 (6)
Co(2)–C(5P)	2.059 (7)	Co(3)–C(10P)	2.124 (6)

(III) Cyclopentadienyl-ring distances

C(1P)–C(2P)	1.407 (10)	C(6P)–C(7P)	1.380 (9)
C(2P)–C(3P)	1.395 (9)	C(7P)–C(8P)	1.425 (9)
C(3P)–C(4P)	1.414 (9)	C(8P)–C(9P)	1.418 (12)
C(4P)–C(5P)	1.408 (9)	C(9P)–C(10P)	1.371 (12)
C(5P)–C(1P)	1.394 (11)	C(10P)–C(6P)	1.392 (9)

(IV) C–H distance and B–H distances in the icosahedral cage

C(1)–H(C1)	1.01 (6)	B(8)–H(B8)	1.07 (6)
B(4)–H(B4)	1.15 (6)	B(9)–H(B9)	1.14 (6)
B(5)–H(B5)	1.11 (6)	B(10)–H(B10)	1.14 (6)
B(6)–H(B6)	1.08 (7)	B(11)–H(B11)	1.09 (6)
B(7)–H(B7)	1.09 (6)	B(12)–H(B12)	1.08 (6)

(V) C–H distances in cyclopentadienyl rings

C(1P)–H(C1P)	0.89 (6)	C(6P)–H(C6P)	0.91 (6)
C(2P)–H(C2P)	1.00 (6)	C(7P)–H(C7P)	0.92 (5)
C(3P)–H(C3P)	0.96 (6)	C(8P)–H(C8P)	0.75 (7)
C(4P)–H(C4P)	1.05 (6)	C(9P)–H(C9P)	0.81 (6)
C(5P)–H(C5P)	0.98 (6)	C(10P)–H(C10P)	0.99 (7)

(VI) Distances within the  $Me_4N^+$  cation

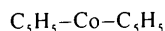
N–C distances			
N–C(1T)	1.475 (10)	N–C(3T)	1.437 (8)
N–C(2T)	1.450 (12)	N–C(4T)	1.505 (11)

Methyl C–H distances

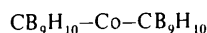
C(1T)–H(1C1T)	0.96 (8)	C(3T)–H(1C3T)	0.81 (8)
C(1T)–H(2C1T)	1.00 (7)	C(3T)–H(2C3T)	1.06 (9)
C(1T)–H(3C1T)	1.10 (7)	C(3T)–H(3C3T)	1.12 (8)
C(2T)–H(1C2T)	1.04 (11)	C(4T)–H(1C4T)	1.09 (9)
C(2T)–H(2C2T)	0.84 (13)	C(4T)–H(2C4T)	1.10 (9)
C(2T)–H(3C2T)	1.25 (11)	C(4T)–H(3C4T)	1.04 (10)

Table 4 (cont.)

(VII) Angles around Co atoms



Type	Range	Mean value	Number of angles
C–Co–C	38.0–40.9	39.4	10
	64.5–67.2	66.2	10



Type	Range	Mean value	Number of angles
Co–C–Co		71.6	1
Co–Co–B	55.8–56.0	55.9	2
	96.2–96.9	96.4	4
Co–Co–C	54.2–54.2	54.2	2
C–Co–B	49.3–49.6	49.4	2
	85.3–85.8	85.5	4
B–Co–B	88.2–88.6	88.4	2
	50.7–51.9	51.2	4
B–B–Co	62.3–67.1	64.4	8
	113.6–119.2	116.9	12
C–B–Co	65.8–66.0	65.9	2
Co–B–Co		68.2	1

(VIII) Cyclopentadienyl-ring angles

Type	Range	Mean value	Number of angles
C–C–Co	68.2–72.2	70.3	20
C–C–C	106.5–110.5	108.0	10

(IX) Cage angles

Type	Range	Mean value	Number of angles
B–B–B	58.7–61.8	60.0	30
	106.0–110.5	108.3	27
B–C–B	61.9–62.0	62.0	2
C–B–B	58.3–59.9	59.0	4
	105.4–106.7	106.1	6

(X) Angles within the  $(CH_3)_4N^+$  cation

C(1T)–N–C(2T)	112.2	C(2T)–N–C(3T)	112.8
C(1T)–N–C(3T)	113.2	C(2T)–N–C(4T)	108.2
C(1T)–N–C(4T)	106.2	C(3T)–N–C(4T)	103.4
H(1C1T)–C(1T)–N	99.3	H(1C1T)–C(1T)–H(2C1T)	104.0
H(2C1T)–C(1T)–N	108.4	H(2C1T)–C(1T)–H(3C1T)	124.5
H(3C1T)–C(1T)–N	105.0	H(3C1T)–C(1T)–H(1C1T)	112.8
H(1C2T)–C(2T)–N	101.0	H(1C2T)–C(2T)–H(2C2T)	142.9
H(2C2T)–C(2T)–N	97.5	H(2C2T)–C(2T)–H(3C2T)	97.8
H(3C2T)–C(2T)–N	73.5	H(3C2T)–C(2T)–H(1C2T)	118.2
H(1C3T)–C(3T)–N	126.4	H(1C3T)–C(3T)–H(2C3T)	119.6
H(2C3T)–C(3T)–N	101.6	H(2C3T)–C(3T)–H(3C3T)	108.1
H(3C3T)–C(3T)–N	114.2	H(3C3T)–C(3T)–H(1C3T)	85.6
H(1C4T)–C(4T)–N	117.9	H(1C4T)–C(4T)–H(2C4T)	115.8
H(2C4T)–C(4T)–N	101.2	H(2C4T)–C(4T)–H(3C4T)	114.7
H(3C4T)–C(4T)–N	104.3	H(3C4T)–C(4T)–H(1C4T)	103.0

distances and mean values of interatomic angles are presented in Table 4. Two Co atoms occupy adjacent vertices with  $Co-Co = 2.430$  Å, close to the average found in analogous bimetallocarboranes (Hoel, Strouse & Hawthorne, 1974; Callahan, Strouse, Sims & Hawthorne, 1974). The distance of the polyhedral C atom to adjacent B atoms (mean 1.719 Å) was important for the confirmation of its identity. The value agrees with the C–B distances in known carborane

Table 5. Important planes in the anion and atomic deviations (Å)

Cyclopentadienyl ring C(1P), C(2P), C(3P), C(4P), C(5P)  
 $0.3385x - 0.7880y + 0.5144z = -3.8711$

C(1P)	+0.006	C(4P)	-0.005
C(2P)	-0.010	C(5P)	-0.001
C(3P)	+0.009		

Cyclopentadienyl ring C(6P), C(7P), C(8P), C(9P), C(10P)  
 $-0.7899x - 0.0529y + 0.6109z = -2.7285$

C(6P)	-0.006	C(9P)	0.000
C(7P)	+0.005	C(10P)	+0.004
C(8P)	-0.003		

Icosahedral plane C(1), B(5), B(7), B(12)

$$-0.8507x + 0.5208y + 0.0712z = 0.7341$$

C(1)	+0.003	B(7)	-0.003
B(5)	-0.003	B(12)	+0.003
Co(3)	-1.217	Co(2)	+1.213
B(4)	-1.436	B(6)	+1.438
B(8)	-1.456	B(11)	+1.459
B(9)	-0.903	B(10)	+0.880

structures. The average B—B distance is longer, 1.787 Å. C—Co is 2.077 Å whereas the average B—Co is 2.104 Å. For terminal H atoms the average B—H = 1.11 and C—H = 1.01 Å. Each Co atom is coordinated to a cyclopentadienyl ring with Co(2)—C(P) = 2.077 and Co(3)—C(P) = 2.073 Å. Table 5 shows that the cyclopentadienyl rings are planar. The mean C—C distance is 1.400, the mean C—H 0.93 Å.

The icosahedral part of the anion has an almost perfect non-crystallographic mirror plane defined by C(1), B(5), B(7) and B(12) (Table 5). The independent bond distances for 'symmetrical' atoms are presented in Table 4. The greatest difference is less than a standard deviation. The perpendicular distances of the polyhedral atoms from the non-crystallographic plane of symmetry are given in Table 5.

For the  $[\text{N}(\text{CH}_3)_4]^+$  ion the parameters of some C atoms, particularly C(2T) and C(4T), did not refine well. Their isotropic temperature parameters were high and the anisotropic parameters of C(2T) and C(4T) were appreciably higher than those of the other C atoms. The respective thermal ellipsoids are elongated with the longest principal axes approximately perpendicular to the N—C bond. In the difference map there exists a continuous positive residual cloud between the positions of C(2T) and C(4T). All these features

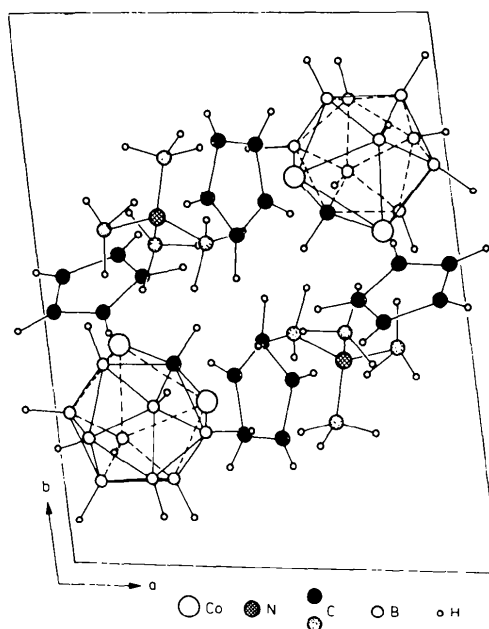


Fig. 2. Packing within the unit cell (one layer from two related by screw axis).

indicate a possible slight disorder in this part of the asymmetric unit. This is probably the reason why the C—N distances ranged from 1.437 to 1.505 Å; similarly the C—H distances in the methyl groups ranged from 0.81 to 1.25 Å.

The shortest interionic H—H distance is 2.20 Å. The packing of ions within the unit cell is indicated in Fig. 2.

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#### References

- ADAMS, R. M. (1972). *Pure Appl. Chem.* **30**, 683–710.  
 CALLAHAN, K. P., STROUSE, C. E., SIMS, A. L. & HAWTHORNE, M. F. (1974). *Inorg. Chem.* **13**, 1397–1401.  
 DOLANSKÝ, J., BAŠE, K. & ŠTÍBR, B. (1977). *Collect. Czech. Chem. Commun.* In preparation.  
 HOEL, E. L., STROUSE, C. E. & HAWTHORNE, M. F. (1974). *Inorg. Chem.* **13**, 1388–1392.  
*International Tables for X-ray Crystallography* (1974). Birmingham: Kynoch Press.