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The Crystal Structure of $Cs(B_9C_2H_{11})_2Co$[1]

BY ALLAN ZALKIN, TED E. HOPKINS, AND DAVID H. TEMPLETON

The crystal structure of $(B_9C_2H_{11})_2CoCs$ has been determined from an X-ray diffraction study on a single crystal specimen. The monoclinic cell, space group C2/c, with a = 11.698 A, b = 7.381 A, c = 21.207 A, and $\beta = 101.73^\circ$ contains four formula units. The structure consists of a cesium cation and a $(B_9C_2H_{11})_2Co^-$ anion. The latter ion consists of two icosahedra sharing one common apex, which is the cobalt atom on a two fold axis. The carbon atoms are disordered among the pentagon of atoms adjacent to the cobalt. All eleven hydrogens, one for each boron and carbon atom, were located as well.

Introduction

The salt, $Cs(B_9C_2H_{11})_2Co$ was synthesized in the laboratory of Professor M. F. Hawthorne[2] at the University of California at Riverside. A crystal structure study was undertaken to confirm the proposed structure of two icosahedra joined at the cobalt apex; this we proved to be true.. The synthesizers of this material had hoped they had produced a compound in which the carbon atoms were not adjacent to each other; unfortunately, we found the carbon atoms to be disordered and therefore could neither affirm or deny this hypothesis.

Experimental

A light brown parallelopiped-shaped crystal of dimensions ~0.15 x 0.15 x 0.30 mm was selected and glued to the end of a pyrex fiber in air. The crystallographic b axis was approximately parallel to the direction of the fiber.

A general Electric XRD-5 X-ray diffraction set-up equipped with a Molybdenum X-ray tube (Mo $K\alpha_1$ λ=0.70926 A), a scintillation counter, a pulse height discriminator, and a quarter-circle Eulerian-cradle type goniostat was used. The X-ray tube was operated at 50 kv and 20 ma; a Zr filter was used on the receiving slit. The crystal was oriented such that the b axis was parallel to the ϕ axis of the instrument. The cell dimensions were obtained from carefully measured 2θ (θ is the Bragg angle) values of the 0k0, h00, and 00ℓ reflections whose $\alpha 1$ and $\alpha 2$ components were resolved. The β angle was measured directly from the angle between the h00 and 00ℓ set of reflections.

A total of 2051 independent intensities were measured, of which 144 were recorded as zero. A stationary-crystal, stationary-counter technique using a 10-sec count for every reflection was used. The maximum 2θ angle was 55° ($\sin\theta/\lambda$=0.651). The maximum observed raw intensity was 46,900 cps for the 200 reflection. Background was plotted as a function of 2θ and these values were used for most of the intensities; in the cases where background was seriously affected by streaking, individual backgrounds were measured. No corrections were made for either absorption or extinction.

Our unpublished least squares program minimizes the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$, where F_o and F_c are the observed and calculated structure factors and w is the weighting factor. All of the non-zero reflections were given equal weights.

Scattering factors for Cs^+, Co, O, C, B, and H were taken from the International Tables.[3] The Cs^+ and Co scattering factors were given $\Delta f'$ corrections, the real part of the anomalous dispersion,[4,5] by the amounts -0.5 and +0.4 electrons, respectively. The imaginary components of the anomalous dispersion, $\Delta f''$, +2.49 and +1.05 electrons for Cs^+ and Co, were introduced into the least-squares calculations as well. The anisotropic temperature factors used have the form $\exp(-\beta 11h^2-\beta 22k^2-\beta 33\ell^2-2\beta 12hk-2\beta 13h\ell-2\beta 23k\ell)$. βij values, in units of A^2, where $Bij = 4\beta ij/a_i^* a_j^*$, are reported in this paper.

Results

Unit Cell and Space Group.- Four formula units of $(B_9C_2H_{11})_2CoCs$ are in the monoclinic space group C2/c. The dimensions of the unit cell are: a = 11.698 ± 0.005 A, b = 7.381 ± 0.004 A, c = 21.207 ± 0.006 A, and β = 101.73 ± 0.05°; the errors are estimates. The calculated X-ray density is 1.692 g/cc. The observed extinctions corespond to C2/c or Cc, and the structure was successfully solved in the centric space group, C2/c.

Determination of the Structure.- The Patterson function readily revealed the locations of the cesium and cobalt atoms. The cesium occupies the special four-fold position on the two-fold axis, and the cobalt is on a center of symmetry at the origin. A least squares refinement on these two atoms alone using anisotropic temperature factors gave an R factor of 0.25, where $R = \Sigma||\underline{F}_o| - |\underline{F}_c|| / \Sigma|\underline{F}_o|$. A difference function phased by these two heavy atoms revealed the positions of the eleven boron and carbon atoms as the eleven largest peaks. Three cycles of full-matrix least squares refinement of the parameters of the heavy atoms with anisotropic temperature factors, and the other eleven atoms as boron with isotropic temperature factors resulted in an R of 0.069.

In attempting to locate the two carbon atoms, we used the two criteria of temperature factors and interatomic distances. Figure 1 shows the framework of the $(B_9C_2H_{11})_2Co^-$ group. When all of these atoms with the exception of Co were refined as borons, the isotropic temperature factors of the pentagon of atoms adjacent to the cobalt, i. e. atoms 2, 3, 4, 5, and 6, ranged from 2.46 A^2 to 2.71 A^2; those of the remaining atoms ranged from 2.96 to 3.24 A^2. Since a carbon atom refined with boron scattering factors would be expected to result in a lower temperature factor, the above results are consistent with the carbon atoms being in the pentagon adjacent to the cobalt. However, the did not uniquely specify which atoms they might be. A better guide to locating the carbons are the interatomic distances. Figure 2 shows the icosahedra spread out with all the interatomic distances in the icosahedra. In our previous study on $B_9C_2H_{11}Re(CO)_3Cs$,[6] which has a boron-carbon network quite similar to this structure, the bond distances were found to be as follows: C-C 1.61 A, C-B 1.72 A, and B-B 1.78 A. In figure 2, the top half of the icosahedra, atoms 7 - 12, appear to have standard B-B distances. In the lower pentagon, atoms 2 - 6, the distances are all more or less B-C type distances. These results as well as the temperature factors indicate the carbons to be present in the lower pentagon in a disordered manner. Since atom 4 had distances to atoms 8 and 9 which are B-B type, we finally chose a model in which atoms 2, 3, 5, and 6 are half borons and half carbons and atoms 4, 7, 8, 9, 10, 11, and 12 are borons. Admittedly this is not exact, but one of the many ways of "playing the game". Various models using different ratios of B and C in the disordered positions were tried; temperature factors were affected, but no significant changes in the distances in the icosahedra structure resulted.

A difference function was calculated, and it indicated the eleven hydrogen atoms among the top seventeen peaks. Six of these top peaks were apparent anisotropies near Cs, Co and B(8).

The final least squares performed with all 24 atoms of the structure included resulted in an R of 0.042. The hydrogen atoms were refined with isotropic temperature factors, and all of the other atoms were refined with anisotropic temperature factors. The real and imaginary components of the anomalous dispersion correction were applied to the Cs and Co atoms. Atoms 2, 3, 5, and 6 in the icosahedra were treated as half boron and half carbon atoms. The B12 and B23 temperature factors of Cs were restrained to zero as required by the symmetry of the special position. Reflections that were observed as zero intensity were given zero weight, all others were given unit weight. The last shift in the parameters in each case was less than one-thousandth of the estimated standard deviation of that parameter. The list of the observed and calculated structure factors is shown in Table I. The final set of parameters are shown in Table II. The Cs, Co, and other atoms are respectively in sets of positions:

4(e): $\pm(0,y,1/4;\ 1/2,1/2+y,1/4)$

4(a): $(0,0,0;\ 0,0,1/2;\ 1/2,1/2,0;\ 1/2,1/2,1/2)$

8(f): $\pm(x,y,z;\ x,\bar{y},1/2+z;\ 1/2+x,1/2+y,z;\ 1/2+x,1/2-y,1/2+z)$.

Table I. OBSERVED AND CALCULATED STRUCTURE FACTORS (x2.0) FOR $(B_9C_2H_{11})_2CoCs^{a}$

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS (X 2.0) OF CS+ (CO (B9)C2)H11)2) -

[illegible]

a Asterisked data are the zero observed and zero weighted reflections.

TABLE II

ATOMIC[a] AND THERMAL PARAMETERS[b] IN $(B_9C_2H_{11})_2CoCs$

Atom	x	y	z	B11	B22	B33	B12	B13	B23
Cs	0[c]	0.4060	1/4[c]	7.46	3.05	4.30	0[c]	-1.11	0[c]
Co(1)	0[c]	0[c]	0[c]	1.75	2.30	2.13	-0.17	0.35	-0.13
BC(2)[d]	0.1224	-0.1774	0.0476	2.5	3.3	2.9	0.3	0.3	0.0
BC(3)[d]	0.1415	0.0369	0.0743	2.5	3.3	3.0	-0.4	-0.1	0.0
B(4)	0.0121	0.1172	0.0904	3.0	2.7	2.2	-0.2	0.4	-0.2
BC(5)[d]	0.4146	0.4396	0.0744	2.9	2.8	2.6	-0.2	1.0	0.0
BC(6)[d]	0.4823	0.2579	0.0470	2.8	2.7	2.7	-0.3	0.5	0.2
B(7)	0.1959	-0.1381	0.1256	2.4	4.0	3.3	-0.1	-0.1	0.5
B(8)	0.1267	0.4838	0.1538	3.5	3.5	2.5	-0.8	-0.1	-0.3
B(9)	0.4810	0.4845	0.1537	3.4	3.2	2.4	-0.4	0.8	-0.2
B(10)	0.4613	0.2594	0.1260	2.8	3.3	2.5	-0.6	0.4	0.2
B(11)	0.0949	-0.3173	0.1087	3.1	3.0	3.4	0.0	0.2	0.3
B(12)	0.0962	-0.1757	0.1761	3.3	3.3	2.8	-0.2	0.0	0.2
H(2)	0.173	-0.233	0.015	2.2[e]					
H(3)	0.197	0.111	0.062	2.5					
H(4)	0.490	-0.262	0.085	1.9					
H(5)	0.319	0.456	0.061	3.0					
H(6)	0.436	0.152	0.019	2.0					
H(7)	0.281	-0.165	0.139	2.1					
H(8)	0.177	0.139	0.186	0.6					
H(9)	0.432	-0.458	0.191	0.4					
H(10)	0.397	0.170	0.142	2.6					
H(11)	0.128	-0.455	0.113	1.1					
H(12)	0.128	-0.227	0.221	0.9					

[a]Estimated standard deviations on the atomic positions for Co, B or BC, and H are ±0.0005 A, ±0.005 A, and ± 0.05 A respectively.

[b]The thermal parameters have the units A^2. The estimated standard deviations on the thermal parameters of Co or Cs, B or BC, and H are ±0.04 A^2, ±0.2 A^2, and ±1.4 A^2 respectively.

[c]Parameter fixed by the space group symmetry.

[d]Half boron and half carbon.

[e]Isotropic B in the case for hydrogen.

Description of Structure.-The structure consists of a Cs^+ cation and a $(B_9C_2H_{11})_2Co^-$ anion. The cesium ion is surrounded by ten hydrogen atoms at distances from 3.00 to 3.34 A; the next nearest neighbors to the cesium atom are two boron atoms, B(10), at 3.67 A.

The framework of the $(B_9C_2H_{11})_2Co^-$ group is shown in Figure 1. The structure consists of two icosahedra in a staggered configuration joined at a common apex, which is the cobalt atom. The two carbon atoms are shown in disordered positions in the pentagon of atoms adjacent to the cobalt, occupying mainly positions 2, 3, 5 and 6. The interatomic distances in the framework are shown in Figure 1.

Each atom with the exception of cobalt in the framework shown in Figure 1 has bonded to it a hydrogen atom. The hydrogen bond lengths are shown in Table III; the differences among them are not experimentally significant.

TABLE III

HYDROGEN BOND DISTANCES IN THE $(B_9C_2H_{11})_2Co^-$ ION[a]

H(2)	1.08 A	H(8)	1.05 A
H(3)	0.93 A	H(9)	1.15 A
H(4)	0.93 A	H(10)	1.11 A
H(5)	1.10 A	H(11)	1.09 A
H(6)	1.06 A	H(12)	1.03 A
H(7)	1.00 A		

[a] Estimated standard deviations of these distances are ±0.06 A.

The above icosahedral structure is very similar to that found in $(B_9C_2H_{11})Fe(C_2H_5)$[7] and in $(B_9C_2H_{11})Re(CO)_3$.[6] where there is no disorder of the carbon atoms. Because of the disorder in $(B_9C_2H_{11})_2CoCs$, we cannot say if the carbon atoms are adjacent or not in each molecule, nor indeed if the crystal contains a single isomer or more than one isomer.

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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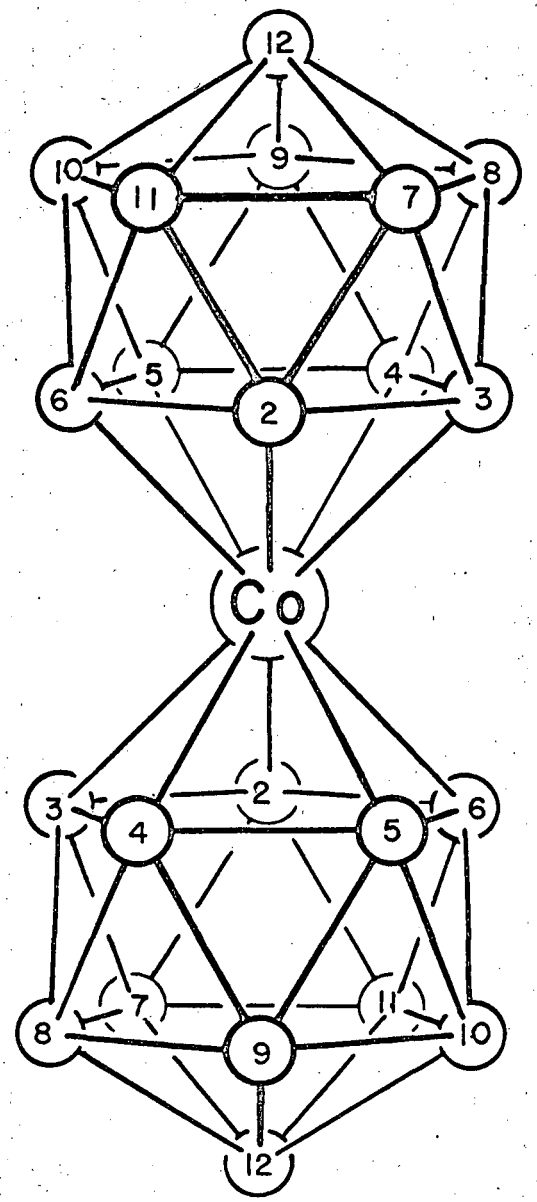

$(B_9C_2H_{11})_2Co^-$

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Figure 1.-Framework of the $(B_9C_2H_{11})_2Co^-$ ion. Hydrogen atoms, which are on each of the atoms with the exception cobalt, are not shown.

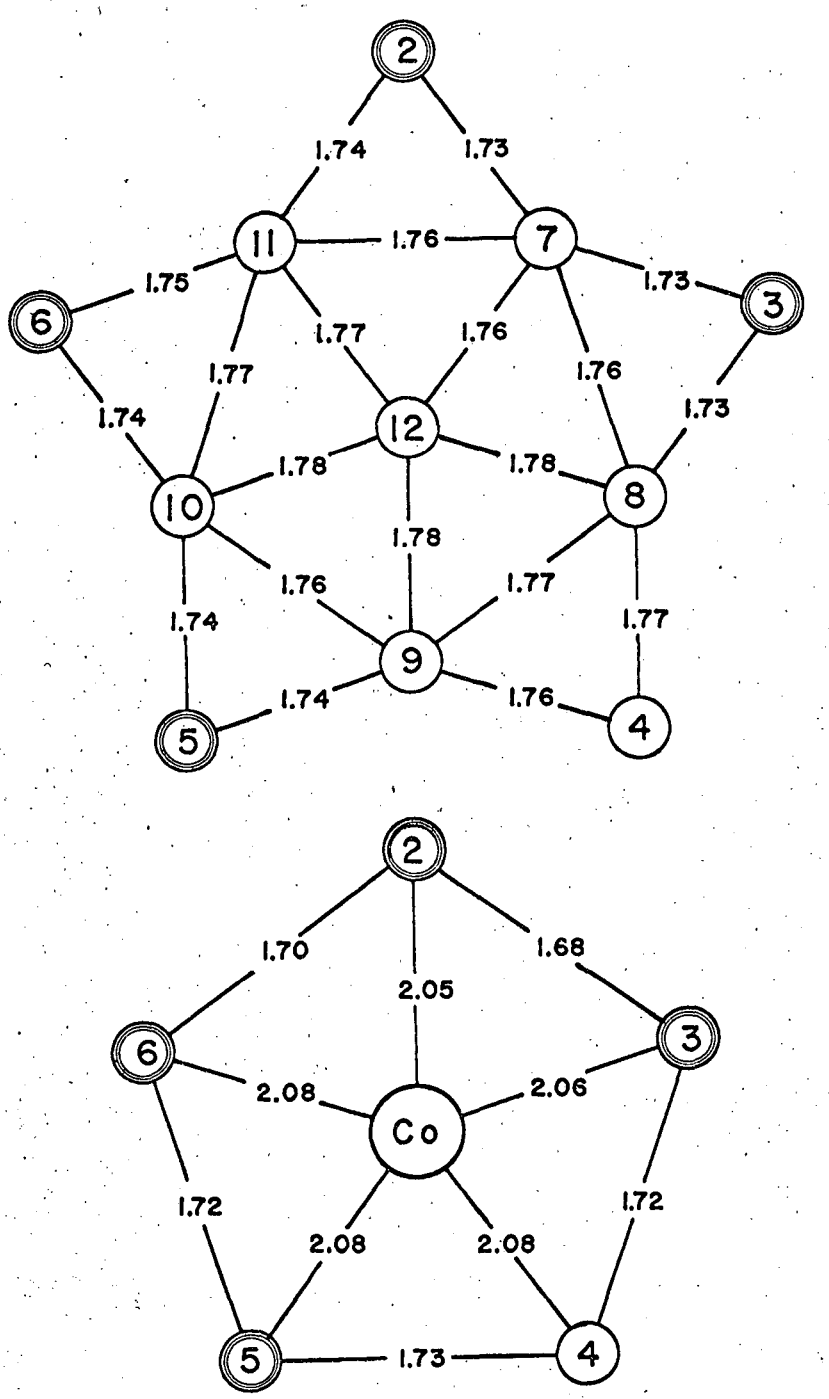

Figure 2.-Interatomic distances in the $(B_9C_2H_{11})_2Co$ icosahedra. Multiple circles indicate the disordered positions containing half boron-half carbon atoms. Single circles represent borons. The estimated standard deviations on these bond lengths are ±0.01 A.