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THE CRYSTAL STRUCTURE OF $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$,
A NICKEL(IV) COMPLEX OF THE DICARBOLLIDE ION

David St. Clair, Allan Zalkin, and David H. Templeton

May 1969

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The Crystal Structure of $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$, a Nickel(IV) complex of the
Dicarbollide Ion¹

By David St. Clair, Allan Zalkin and David H. Templeton

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

Abstract

The crystal structure of the neutral molecule, 3,3'-commo-bis[undeca-hydro-1,2-dicarpa-3-nickela-closo-dodecaborane], $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$, has been determined from 3242 independent X-ray data obtained from a single-crystal using a scintillation counter and the θ - 2θ scanning technique. The monoclinic unit cell has dimensions $a = 13.371 \text{ \AA}$, $b = 10.398 \text{ \AA}$, $c = 13.556 \text{ \AA}$, and $\beta = 119.16^\circ$. The space group is $P2_1/c$. There are 4 molecules in the unit cell and the calculated density is 1.31 g/cc. The model was refined to a conventional discrepancy factor of $R = 0.035$. The molecule has the shape of two icosahedra, each composed of nine boron atoms, two carbon atoms and a nickel atom, which have one vertex position occupied by the nickel shared in common. The positions of the carbon atoms in the cage were determined and all hydrogen atoms were located. The carbon atoms in opposite cages are as close to each other as is possible in the staggered configuration. The molecule has point symmetry C_2 . There are two enantiomorphic rotational isomers present in the crystal.

Introduction

Another in the series of transition metal complexes of the dicarbollide ion, $(B_9C_2H_{11})^{-2}$, has been prepared^{2,3}. This complex, $Ni(B_9C_2H_{11})_2$,

(2) L. F. Warren and M. F. Hawthorne, J. Am. Chem. Soc., **89**, 470(1967).

(3) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879(1968).

3,3'-comno-bis[undecahydro-1,2-dicarpa-3-nickela-closo-dodecaborane]⁴,

(4) This name is based on the ACS-approved nomenclature rules given in Inorg. Chem., **7**, 1945(1968). The name given by Warren and Hawthorne in their original publication, reference 2, is bis- π -(3)-1,2-dicarbollylnickel(IV).

is a neutral molecule in which the nickel is in a formal +4 valence state. Warren and Hawthorne predicted the structure as having the nickel ion sandwiched between the open five fold faces of two $(B_9C_2H_{11})^{-2}$ icosahedral fragments. Because of the unusual chemical and spectral properties of this compound, observed for only this molecule and an analogous $Pd(B_9C_2H_{11})_2$ neutral molecule⁵, an unusual structure was

(5) L. F. Warren and M. F. Hawthorne, J. Am. Chem. Soc., **90**, 4823(1968).

expected.

In this paper, we report the results of a single-crystal X-ray

analysis which confirms the sandwich type structure in the molecule, shown in Figure 1. We show that there are two enantiomorphic rotational configurations present in the crystal and that the cages are staggered. The structure is novel among the unsubstituted metallocarboranes containing two dicarbollide ions in that the pairs of carbon atoms in opposite cages are as close to each other as is possible in this staggered configuration, so that the molecule has only the symmetry of a 2-fold axis. A similar configuration of carbon atoms has been observed, however, in a double-icosahedral-cage cobalt metallocarborane in which the two cages are linked by a S - C - S bridge⁶, and in a metallocarborane containing

(6) M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *ibid.*, 21, 1222(1969).

three linked icosahedra⁷.

(7) D. St. Clair, A. Zalkin, and D. H. Templeton, submitted for publication in *Inorg. Chem.*

Experimental

The yellow crystals, as sent to us by Professor Hawthorne of the University of California, Riverside, were used. One of dimensions 0.17 x 0.15 x 0.12 mm was glued to the tip of a glass fiber in the open air with its b axis parallel to the rotation axis of the fiber.

Approximate cell dimensions and space group possibilities were determined from oscillation and Weissenberg photographs taken with copper radiation ($\text{Cu K}\alpha_1$; $\lambda = 1.5405 \text{ \AA}$). Space group absences were checked and from measurements on the $h00$, $0k0$, and $00l$ reflections, accurate unit cell dimensions were determined using a manually operated General Electric XRD-5 diffractometer. Intensity data were collected using a card input, card output automated General Electric diffractometer equipped with a quarter circle, Eulerian cradle goniostat. Copper $\text{K}\alpha$ radiation from an X-ray tube operated at 35 kv and 16 ma was used. A 0.003 inch thick nickel $\text{K}\beta$ filter was placed between the crystal and the receiving slit. The intensity of the scattered radiation was measured with a scintillation counter equipped with a pulse height discriminator. The integrated intensity of each reflection was measured by the θ - 2θ scan technique by scanning from 0.65° below the 2θ angle at which $\text{K}\alpha_1$ was diffracted at a rate of 1 degree/minute until the 2θ value reached 0.65° above the 2θ angle at which $\text{K}\alpha_2$ was diffracted. Two ten-second background counts were taken with the apparatus stationary at 0.40° below and above the 2θ angles at which scanning was begun and ended, respectively. Three moderate intensity reflections were remeasured periodically to check for crystal decomposition or machine malfunctions but no significant variation was observed.

All calculations were done using a CDC 6600 computer. The raw data were converted into intensities, \underline{I} , and standard deviations, $\sigma(\underline{I})$, according to the equations:

$$\underline{I} = \underline{C} - \frac{t_c}{2t_b}(B_1 + B_2) \quad \text{and} \quad \sigma^2(\underline{I}) = \underline{C} + \frac{t_c^2}{4t_b^2}(B_1 + B_2)$$

where \underline{C} is the total count accumulated while scanning across a reflection for a time, t_c , and B_1 and B_2 are the background counts obtained in time, t_b . When a reflection was measured more than once, the intensities were averaged and its standard deviation was set equal to the greater of $\frac{1}{n}(\sum \sigma_i^2)^{\frac{1}{2}}$ or $\frac{1}{n-1}(\sum \Delta_i^2)^{\frac{1}{2}}$, where σ_i and Δ_i are the standard deviation of the i^{th} measurement and the deviation of the i^{th} measurement from the average, respectively, and n is the number of measurements of the i^{th} reflection. To reduce the weight assigned to the large intensities, an additional term, $(0.03\underline{I})^2$, was included in the calculation of $\sigma^2(\underline{F}^2) = (\text{LP})^2[\sigma^2(\underline{I}) + (0.03\underline{I})^2]$.

All except 16 of the \underline{hkl} and $\underline{hk\bar{l}}$ reflections within the sphere of reflection bounded by $\sin\theta/\lambda = 0.6216$ ($2\theta_{\text{max}} = 147^\circ$) were measured. Excluding systematic space group absences, there were 3242 independent data of which 508 had an intensity less than its standard deviation including 232 reflections measured to be zero.

The absorption coefficient for this compound is $\mu = 13.7 \text{ cm}^{-1}$. No correction for absorption effects was applied. It is estimated that absorption effects introduce a maximum error of 8% in the intensity data.

Lorentz and polarization factors were applied and the data were converted to structure factors. Refinements were done using our unpub-

lished version of a full matrix least squares program which minimizes the quantity $\sum_w (|F_o| - |F_c|)^2 / \sum_w |F_o|^2$, where F_o and F_c are the observed and calculated structure factors and w is the weighting factor. In the original refinements, $w = 1$ was used for all reflections but for the final refinements, $w = [\sigma(F)]^{-2}$ was used where $\sigma(F) = [\sigma(F^2)]^{\frac{1}{2}}$, if $I \leq \sigma(I)$ and $\sigma(F) = F - [F^2 - \sigma(F^2)]^{\frac{1}{2}}$, if $I > \sigma(I)$. Anisotropic temperature factors used have the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. All atoms were considered to be in their neutral valence state. The scattering factors of Cromer and Waber⁸ were used

(8) D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104(1965).

for all atoms except hydrogen whose scattering factors are those of Stewart, Davidson and Simpson⁹. Cromer's corrections¹⁰ for anomalous

(9) R. F. Stewart, E. R. Davidson and W. T. Simpson, Table II, J. Chem. Phys., 42, 3175(1965).

(10) D. T. Cromer, Acta Cryst., 18, 17(1965).

dispersion applied to the scattering factors of the nickel are $\Delta f' = -3.20$ and $\Delta f'' = +0.67$ electrons. The stereoscopic pair drawings were prepared using Johnson's ORTEP program¹¹.

(11) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Crystal Data

The crystals are monoclinic with unit cell dimensions, measured at room temperature ($\sim 22^\circ$), $\underline{a} = 13.371 \pm 0.003 \text{ \AA}$, $\underline{b} = 10.398 \pm 0.005 \text{ \AA}$, $\underline{c} = 13.556 \pm 0.003 \text{ \AA}$, $\beta = 119.16 \pm 0.04$ degrees. There are four molecules of $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$ in the unit cell. The calculated density, $\rho = 1.31 \text{ g/cc}$, agrees well with the observed density, $\rho = 1.30 \text{ g/cc}$, measured by flotation.

The extinction rules found, $0k0$, $\underline{k} = 2n$ and $h0\ell$, $\underline{\ell} = 2n$, are characteristic of space group $P2_1/c$. All atoms lie on the general symmetry equivalent positions, $\pm(\underline{x}, \underline{y}, \underline{z})$ and $\underline{x}, \underline{\frac{1}{2}} - \underline{y}, \underline{\frac{1}{2}} + \underline{z}$.

Determination of the Structure

There are four general symmetry equivalent positions in this space group and there are four molecules of $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$ in the unit cell; thus, the asymmetric unit is one complete molecule. Since the pattern of strong and weak intensities was dominated by the nickel atom, its coordinates were readily found by testing trial coordinate values in the structure factor equation. The conventional R value, $R = \frac{\sum |F_o| - \sum |F_c|}{\sum |F_o|}$, based on a least squares refinement of an overall scale factor and three coordinates and an isotropic thermal parameter for the nickel, stopped at $R = 0.46$. A Fourier synthesis using phases calculated from the nickel atom only, contained peaks, some rather poorly resolved, corresponding to the twenty-two carbon and boron atoms. When these atoms, all with the scattering power of boron, were added to the refinement, the R value dropped to 0.14. Thermal parameters and bond distances gave exceptionally clear indications of the positions of the two carbon atoms in each cage, and in all further refinements, these atoms were given the scattering power of carbon. When some blunders in the intensity data were removed and when the anomalous dispersion corrections were applied, full matrix least squares refinement of a scale factor, three positional coordinates and six anisotropic thermal parameters for each of the twenty-three atoms gave $R = 0.086$ for all 3242 data. On a difference Fourier using phases calculated from the atoms in this refinement appeared all of the twenty-two hydrogen atoms. When three positional parameters and an isotropic thermal parameter for each hydrogen were included and when weighting factors derived from the sigmas were used, full matrix least squares refinement gave $R = 0.072$ for all 3242 data. It was noticed that all of the five maximum

intensity reflections were observed much too low, suggesting that their counting rates exceeded the capacity of the scintillation counter; therefore, they were given zero weight in all further least squares refinement. The final series of refinement was carried out on an overall scale factor, three positional parameters and six anisotropic thermal parameters for each of the twenty-three non-hydrogen atoms and three positional parameters and an isotropic thermal parameter for each of the twenty-two hydrogen atoms. The five maximum intensity reflections and all reflections for which $I < \sigma(I)$ were given zero weight. This refinement gave the conventional R values of $R = 0.035$ for the 2724 non-zero-weighted data, and $R = 0.051$ calculated using all 3242 data. The weighted R value, $R_2 = [\sum W(|F_o| - |F_c|)^2 / \sum W|F_o|^2]^{1/2}$, reached $R_2 = 0.031$. The standard deviation of observation of unit weight, given by $[\sum W(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$, where n and p are the number of data and the number of parameters, respectively, was 1.2. R.M.S. averages of $(|F_o| - |F_c|) / \sigma(F)$ taken over small intensity intervals approximated this value of 1.2 over the entire intensity range. No parameter shifted by more than 5 % of its estimated standard deviation of the final cycle of refinement.

Results and Discussion

Final values for atomic positions and thermal parameters are given in Table I for all the non-hydrogen atoms and in Table II for the hydrogen atoms. The observed and calculated structure factors are shown in Table III.

As shown by the stereoscopic pair drawing in Figure 2, this neutral molecule is a double-cage carborane having the nickel atom sandwiched between the cages by bonding to the open five-fold faces of the two icosahedral fragments. Each of the carbon and boron atoms in the cages has a hydrogen atom pointing out radially from the cage approximately along a line from the atom to which it is attached to the atom directly opposite it in the cage. The carbon pairs in the cages on opposite sides of the metal are as close as is possible with the cages staggered. The carbons allow only C_2 point symmetry for the molecule. This lack of reflection and inversion symmetry permits the existence of enantiomorphous rotational isomers.

An interesting feature of the structure may be seen by passing four planes through the molecule, each containing five atoms. Label the plane through atoms B(5), B(6), B(9), B(11) and B(12) of Cage 1 as plane 1 and the plane through the same atoms of Cage 2 as plane 4. Let atoms C(1), C(2), B(4), B(7) and B(8) of Cage 1 form plane 2 and let the same atoms in Cage 2 form plane 3. Then, planes 2 and 3 are tipped from a parallel arrangement in such a way that the distance between the carbon pairs on opposite sides of the nickel is increased. Thus, the distance from C(1) in Cage 1 to C(1) in Cage 2 is 3.21 Å while the distance from B(8) in Cage 1 to B(8) in Cage 2 is 3.00 Å.

Table I

Positional Parameters($\times 10^5$) and Thermal Parameters($\times 10^2$) for all Non-hydrogen Atoms^{a, b, c}

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B₁₁</u>	<u>B₂₂</u>	<u>B₃₃</u>	<u>B₁₂</u>	<u>B₁₃</u>	<u>B₂₃</u>
Ni	25452(2)	06001(3)	25232(2)	204(1)	196(1)	186(1)	-03(1)	98(1)	-09(1)
Atoms in Cage 1									
C(1)	26879(15)	25130(17)	21672(15)	314(7)	222(7)	237(7)	-01(6)	162(6)	09(6)
C(2)	13990(15)	20935(19)	17896(15)	259(7)	285(9)	218(7)	40(6)	99(6)	-16(6)
B(4)	36258(18)	20898(21)	35311(18)	245(8)	246(9)	245(8)	-22(7)	106(7)	-22(7)
B(5)	31486(19)	37147(23)	31314(19)	341(10)	223(10)	306(9)	-20(8)	154(8)	-37(7)
B(6)	17313(20)	37024(23)	19900(19)	383(10)	251(10)	280(9)	71(8)	148(8)	06(8)
B(7)	12810(17)	13113(22)	28568(18)	244(8)	303(9)	289(9)	04(7)	156(7)	-25(7)
B(8)	27455(18)	13394(22)	40670(17)	304(8)	290(10)	198(8)	04(7)	136(7)	-11(7)
B(9)	31460(19)	30034(22)	43161(18)	322(9)	283(10)	232(8)	05(8)	103(7)	-56(7)
B(10)	19789(20)	39795(23)	33749(19)	383(10)	276(10)	261(9)	55(8)	137(8)	-44(7)
B(11)	08508(18)	29553(23)	24523(18)	273(9)	344(11)	276(9)	77(8)	119(7)	-45(8)
B(12)	17116(19)	25312(23)	38973(18)	333(9)	340(10)	246(8)	30(8)	166(7)	-41(8)
Atoms in Cage 2									
C(1)	24025(16)	-03074(18)	10997(14)	328(8)	255(8)	199(7)	44(6)	121(6)	07(6)
C(2)	37008(15)	-02532(18)	21221(15)	273(7)	268(8)	263(7)	20(6)	163(6)	11(6)

Table I(continued)

B(4)	14645(19)	-08839(22)	15061(19)	264(8)	253(10)	276(9)	-40(7)	94(7)	-59(7)
B(5)	19396(20)	-18226(24)	07177(19)	387(10)	282(10)	265(9)	26(9)	102(8)	-64(8)
B(6)	33589(20)	-13955(22)	10892(19)	420(10)	293(10)	265(9)	90(8)	201(8)	08(7)
B(7)	37965(18)	-07933(21)	33719(17)	263(8)	249(9)	201(8)	34(7)	101(7)	10(7)
B(8)	23365(18)	-12736(20)	30031(18)	326(9)	222(8)	290(9)	-22(7)	186(8)	17(7)
B(9)	19171(22)	-24717(24)	19148(21)	410(11)	232(10)	386(11)	-47(8)	192(10)	-34(8)
B(10)	30930(22)	-27930(23)	16777(20)	437(11)	257(10)	338(10)	49(9)	183(9)	-21(8)
B(11)	42256(18)	-17369(23)	25368(18)	306(9)	286(9)	292(9)	80(8)	158(7)	21(8)
B(12)	33653(21)	-24149(23)	30686(19)	399(10)	238(10)	300(9)	47(8)	187(8)	49(8)

(a) The numbering system is shown in Figure 1.

(b) Errors estimated by least squares for the least significant digits are given in parentheses following the parameter.

(c) The anisotropic thermal parameters, \underline{B} , in units of \AA^2 , are given by $\underline{B}_{ij} = 4\beta_{ij}/\underline{a}_i^* \underline{a}_j^*$, where \underline{a}_i^* is the length of the i^{th} reciprocal cell dimension.

Table II

Hydrogen Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10$)^{a, b}

Atom	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u>
Atoms in Cage 1				
H(1)	2916(14)	2507(16)	1632(14)	22(4)
H(2)	0962(15)	1870(20)	1037(16)	32(4)
H(4)	4509(15)	1890(18)	3779(15)	30(4)
H(5)	3763(16)	4379(17)	3133(15)	29(4)
H(6)	1440(15)	4284(17)	1268(15)	27(4)
H(7)	0571(15)	0643(16)	2679(15)	30(4)
H(8)	3071(16)	0664(17)	4780(16)	33(4)
H(9)	3748(16)	3302(19)	5189(16)	38(4)
H(10)	1826(15)	4912(20)	3635(15)	31(4)
H(11)	-0046(15)	3131(18)	2033(15)	31(4)
H(12)	1341(16)	2537(18)	4468(15)	36(4)
Atoms in Cage 2				
H(1)	2193(16)	0348(18)	0554(16)	31(4)
H(2)	4163(16)	0451(18)	2099(16)	34(5)
H(4)	0619(17)	-0569(18)	1087(17)	38(5)
H(5)	1340(16)	-1983(20)	-0192(17)	41(5)
H(6)	3670(16)	-1256(19)	0486(16)	40(5)
H(7)	4462(16)	-0493(17)	4125(15)	29(4)
H(8)	2015(15)	-1369(18)	3580(15)	30(4)
H(9)	1300(17)	-3179(21)	1842(17)	43(5)
H(10)	3260(17)	-3753(20)	1466(17)	40(5)
H(11)	5148(15)	-1888(17)	2882(15)	28(4)
H(12)	3679(15)	-3132(19)	3721(15)	32(4)

Table II(continued)

- (a) The number in the atom label refers to the number of the position in Figure 1 of the atom to which the hydrogen is bonded.
- (b) Errors estimated by least squares for the least significant digits are given in parentheses following the parameter.

Table III

Observed and Calculated Structure Factors. Each datum given zero weight in the final refinement is indicated with an asterisk.

DERIVED AND CALCULATED STRUCTURE FACTORS
FCAD0.001 1968

Table with multiple columns containing numerical data, likely representing structure factors and calculated values. The data is organized in a grid-like format with various numerical entries and some text labels.

H.K.	9	4	-9	49	50	H.K.	10	2	-4	17	16	-6	9	10*	-13	78	77	2	69	68	2	16	15	-8	51	53	-6	5	4*	H.K.	12	8	-13	24	20	-10	25	25	-3	0	5*	-12	70	21						
-14	15	16	-8	19	17	-16	36	36	-3	79	80	-5	33	31	-12	0	6*	3	25	26	3	0	2*	-7	18	12	-7	75	75	-10	71	73	-12	60	61	-9	26	25	-2	48	49	-11	18	18						
-13	10	10	-7	69	68	-15	19	18	-2	37	14	-4	24	22	-11	51	50	6	67	66	H.K.	11	7	-6	40	42	-6	16	14	-9	14	11	-11	38	39	-8	9	9	-1	26	26	-10	48	47	-9	25	26			
-12	24	24	-6	76	76	-16	46	46	-1	37	24	-2	26	28	-10	19	20	H.K.	11	4	-12	43	46	-8	20	16	-8	20	16	-8	80	81	-8	66	-12	67	69	-7	36	38	0	46	46	-9	25	26				
-11	7	6*	-5	73	71	-13	46	47	0	16	14	-2	11	7	-9	40	70	-15	16	13	-11	70	69	-4	18	22	-4	10	14	-7	5	2*	-9	35	34	-6	32	32	H.K.	14	4	-8	51	51	2	11	7			
-10	18	19	-4	11	12	-12	78	79	1	75	71	-1	27	28	-8	20	18	-14	23	23	-10	36	36	-5	21	22	-3	71	71	-6	88	87	-8	49	50	-5	53	53	-13	14	35	-7	11	7						
-9	3	2*	-3	58	60	-11	70	70	2	9	2	0	4	10*	-7	91	89	-13	18	14	-9	31	32	-2	25	24	-2	15	10	-5	13	-7	22	24	-4	39	38	-12	11	9	-6	15	14							
-8	26	27	-2	1	1*	-10	64	67	3	91	91	1	26	26	-6	0	8*	-12	25	26	-8	12	7	-1	23	22	-1	75	74	-4	106	106	-6	39	38	-3	46	46	-11	53	53	-5	20	21						
-7	0	6*	-1	15	10	-9	57	59	4	15	13	2	14	13	-5	53	50	-11	14	13	-7	33	34	0	18	16	0	15	12	-3	9	10	-5	27	23	H.K.	15	0	-10	9	5	-4	9	9						
-6	9	10*	0	19	17	-8	67	65	5	39	39	3	0	3*	-4	27	27	-10	4	13*	-6	40	39	1	0	5*	1	109	109	-2	50	52	-4	66	65	-14	72	73	-9	36	37	-3	41	41						
-5	12	15	-1	11	4	-7	100	100	H.K.	10	5	H.K.	10	8	-3	83	84	-9	25	26	-5	69	70	2	0	10*	7	5	4*	H.K.	13	0	-3	27	27	-12	40	45	-8	0	11*	-2	6	2*						
-4	12	14	-2	12	14	-6	148	148	-15	13	13	-12	43	44	-2	42	40	-8	0	6*	-4	54	53	3	7	11*	3	68	67	-14	14	15	-2	81	79	-10	40	42	-7	27	26	H.K.	15	3	3	3				
-3	26	25	H.K.	9	10	-5	106	107	-14	8	2	-11	20	16	-1	106	103	-7	26	22	-3	71	72	4	15	17	H.K.	12	5	-12	16	16	-1	40	43	-8	53	54	-6	21	18	-12	35	37						
-2	28	25	-9	16	18	-8	81	-13	64	61	-10	64	64	0	26	26	6	0	3*	-2	28	25	H.K.	12	2	-14	0	4*	-10	19	19	0	54	53	-6	65	65	-5	46	46	-11	19	14							
-1	9	1*	-8	13	10	-3	102	102	-12	14	16	-9	13	14	1	56	57	-5	15	16	-1	55	56	-15	13	10	-13	28	28	-9	31	31	1	36	35	-4	54	54	-4	0	4*	-10	46	45						
0	42	42	-7	13	13	-2	74	74	-11	40	39	-8	59	60	2	5	11*	-4	6	8*	0	24	25	-14	26	27	-12	6	7*	-8	33	34	H.K.	13	4	-7	29	30	-3	38	38	-9	16	13						
1	16	16	-6	8	8	-1	98	96	-10	0	7*	-7	11	9	-3	35	34	-3	0	11*	1	35	35	-13	26	28	-11	18	17	-4	32	32	-14	14	13	0	37	35	-2	8	9	-8	42	44						
2	15	17	-5	17	17	0	83	81	-9	22	21	-6	81	81	4	15	17	-2	0	7*	0	24	20	-12	61	62	-10	24	25	-2	24	24	-13	12	11	H.K.	14	1	-1	42	43	-1	16	20						
3	20	18	-4	0	3*	1	52	54	-8	18	22	-5	17	19	5	45	46	-1	12	10	H.K.	11	8	-11	46	47	-9	2	9*	0	14	14	-12	9	9	-14	10	13	H.K.	14	5	-6	37	36						
4	0	10*	-3	39	36	2	47	47	-7	25	20	-4	117	116	H.K.	11	2	0	31	29	-11	6	9*	-10	72	72	-8	27	25	2	13	14	-11	13	14	-13	9	11	-12	25	24	-5	70	21						
5	4	4*	-2	4	1*	3	38	39	-6	27	27	-3	9	8	-16	19	19	1	38	35	-10	12	10	-9	97	95	-7	43	43	H.K.	13	1	-10	19	20	-12	13	12	-11	44	45	-4	68	67						
H.K.	9	7	-1	15	17	4	46	44	-5	24	26	-2	71	71	-15	7	11*	2	56	56	-9	22	23	-8	83	82	-6	25	25	-11	7	9*	0	22	25	-11	7	9*	0	21	19	-3	28	29						
-13	80	80	0	8	10	5	31	32	-4	30	29	-1	15	15	-14	9	5	3	33	35	-8	0	2*	-7	69	68	-5	29	28	-14	22	25	-8	56	54	-10	-9	8	-7	4	1*	H.K.	15	4	4	4				
-12	74	74	H.K.	10	0	6	37	36	-3	6	4*	0	35	35	-13	16	16	4	34	32	-7	0	2*	-6	59	56	-4	18	18	-13	67	66	-7	24	23	-9	25	22	-8	11	10	-11	6	2*						
-11	124	124	-14	86	85	H.K.	10	3	-2	16	17	1	5	3*	-12	0	1*	H.K.	11	5	-6	4	1*	-5	50	49	-3	14	14	-12	6	9*	-6	45	45	-8	17	11	-7	27	26	-10	8	3						
-10	88	87	-14	110	105	-16	10	15	-1	14	13	2	29	31	-11	13	15	-14	33	35	-5	6	9*	-4	18	16	-3	12	13	-11	63	63	-5	20	21	-7	38	37	-6	19	20	-9	1	3*						
-9	80	79	-12	18	15	-15	7	9*	0	20	19	H.K.	10	9	-10	14	1	-13	0	3*	-4	30	28	-3	55	52	-1	16	13	-10	16	18	-4	0	2*	-6	20	16	-5	17	17	-8	2	2*						
-8	34	33	-10	40	37	-14	17	16	1	0	2*	-10	25	25	-8	23	25	-12	44	45	-3	9	12	-2	29	28	0	27	27	-9	95	95	-3	17	20	-5	19	21	-4	20	19	-7	16	10						
-7	54	58	-8	74	74	-13	0	7*	2	25	25	-8	6	1*	-8	37	37	-11	17	15	-2	19	19	-1	14	13	-8	39	38	-2	0	1*	-4	10	11	-3	4	4*	-6	6	8*									
-6	45	45	-6	29	31	-12	23	27	3	19	21	-8	26	23	-7	70	70	-10	67	67	-1	13	14	0	20	23	2	25	25	-9	91	96	-1	31	29	-3	13	11	-2	12	-4	18	17							
-5	66	68	-4	34	36	-11	4	20*	4	7	8*	-7	0	2*	-6	19	20	-9	31	29	0	8	4	1	2	4*	H.K.	12	6	-6	43	43	0	10	1	-2	12	8	H.K.	14	6	-10	4	8	7	H.K.	15	5	5	5
-4	47	48	-7	136	140	-10	16	9	5	20	19	-6	13	16	-9	0	13	16	-4	46	44	-7	28	27	-9	61	61	3	12	12	-12	19	18	-4	32	32	H.K.	13	5	0	7	6	8*	-9	17	6				
-3	58	55	0	112	111	-9	19	11	H.K.	10	6	-5	13	15	-4	46	44	-7	28	27	-9	61	61	3	12	12	-12	19	18	-4	32	32	H.K.	13	5	0	7	6	8*	-9	17	6								
-2	23	25	2	70	70	-8	12	10	-14	29	30	-4	2	2*	-3	43	42	-6	101	96	-8	5	9*	H.K.	12	3	-11	24	24	-3	44	45	-13	17	17	H.K.	14	5	2	8	15	14	-8	12	12					
-1	73	73	4	71	70	-7	36	35	-13	64	65	-3	24	24	-2	56	53	-5	27	25	-7	62	65	-15	9	1	-10	13	3	-23	23	-12	37	39	-14	35	35	-7	23	20	-7	2	1*							
0	41	39	6	93	93	-6	15	13	-12	51	50	-2	15	14	-1	4	1*	-4	102	103	-6	73	77	-14	15	12	-9	22	19	-1	32	33	-11	31	30	-13	29	28	-4	26	25	-6	35	35						
1	81	81	H.K.	10	1	-5	26	24	-11	88	89	-1	11	13	0	0	8*	-3	19	20	-5	19	20	-6	13	16	15	-8	19	13	0	12	12	-10	22	23	-12	54	55	-5	35	36	-5	7	6					
2	35	36	-16	14	12	-4	7	1*	-10	48	48	0	20	20	1	29	29	-2	89	91	-4	1	13	-12	24	24	-7	27	28	1	20	19	-8	26	26	-11	41	39	-4	22	25	H.K.	16	0	10	10				
3	42	41	-15	6	4*	-3	90	89	-9	55	55	H.K.	10	10	2	9	9	-1	16	15	-3	52	54	-10	26	25	-6	32	34	2	0	4*	-8	36	38	-10	72	73	H.K.	15	0	-10	33	33						
4	6	2*	-14	2	9*	-2	42	45	-8	38	39	-7	26	26	3	14	11	0	82	81	-2	12	6	-10	20	21	-5	60	60	H.K.	13	2	-7	16	15	-9	81	78	-12	12	9	-8	24	24						
H.K.	9	8	-13	0	3*	-1	67	67	-7	70	70	-6																																						

The vector from Ni to B(10) of Cage 1 is parallel to the corresponding vector, Ni to B(10) in Cage 2, so the molecule as a whole is not bent. But, taking the best least squares planes through the atoms, plane 2 makes an angle of 6° with plane 3 and plane 1 makes an angle of 3° with plane 4. The atoms assigned to planes 2 and 3, however, are not exactly planar. If only the three boron atoms, B(4), B(7) and B(8) are included in the calculation of these planes, the angle between them is only 2° . The carbon atoms are displaced out of these planes toward B(6) by 0.09 Å in Cage 1 and by 0.07 Å in Cage 2. Thus, the carbon atoms in each cage are displaced approximately toward the geometric center of each twelve-membered cage, up toward B(6) but in toward the center until the C - Ni distances are less than the B - Ni distances. That planes 1 and 4 are not parallel is probably due to shifts of the atoms in these planes, especially B(6), as compensation for the displacements of the carbon atoms.

Interatomic distances are given for all atoms except hydrogens in Table IV. The distances between the hydrogen atoms and the carbons or borons to which they are attached are given in Table V. Since the asymmetric unit consists of both cages of one molecule, for every distance in one cage there is another independent value of an equivalent distance in the other cage. Having two values for every type of bond distance allows one to calculate average estimated errors based on the discrepancies between each pair of distances by the equation, $\sigma = (\sum \Delta_i^2 / \underline{n})^{\frac{1}{2}}$, where Δ_i is the difference between the bond distance in one cage and the corresponding bond distance in the other cage and where \underline{n} is the number of pairs. This gives $\sigma = \pm 0.004$ Å on the Ni to C or B distances,

Table IV

Bond Distances (\AA)^a Excluding Hydrogen

Atom 1	Atom 2	Cage 1	Cage 2
Ni	C(1)	2.077	2.072
Ni	C(2)	2.065	2.071
Ni	B(4)	2.105	2.104
Ni	B(7)	2.086	2.085
Ni	B(8)	2.120	2.115
C(1)	C(2)	1.601	1.610
C(1)	B(4)	1.710	1.706
C(1)	B(5)	1.692	1.680
C(1)	B(6)	1.710	1.713
C(2)	B(6)	1.718	1.720
C(2)	B(7)	1.732	1.729
C(2)	B(11)	1.670	1.675
B(4)	B(5)	1.794	1.778
B(4)	B(8)	1.832	1.827
B(4)	B(9)	1.764	1.753
B(7)	B(8)	1.843	1.833
B(7)	B(11)	1.802	1.791
B(7)	B(12)	1.772	1.765
B(8)	B(9)	1.794	1.799
B(8)	B(12)	1.786	1.786
B(5)	B(6)	1.769	1.767
B(5)	B(9)	1.770	1.771
B(6)	B(11)	1.761	1.762

Table IV(continued)

B(9)	B(12)	1.783	1.802
B(11)	B(12)	1.777	1.774
B(10)	B(5)	1.770	1.770
B(10)	B(6)	1.764	1.775
B(10)	B(9)	1.776	1.783
B(10)	B(11)	1.771	1.771
B(10)	B(12)	1.773	1.781

(a) Standard deviations calculated from the least squares estimates of the errors in coordinates are the following: ± 0.002 Å on all distances to Ni; ± 0.002 Å on C(1) - C(2) in each cage; ± 0.004 Å on B(9) - B(10) and B(9) - B(12) in Cage 2; and ± 0.003 Å on all others.

Table V

Bond Distances (\AA) Between Atom and its Hydrogen^a

<u>Atom</u>	<u>Cage 1</u>	<u>Cage 2</u>
C(1)	0.91	0.94
C(2)	0.93	0.97
B(4)	1.08	1.04
B(5)	1.07	1.11
B(6)	1.05	1.09
B(7)	1.11	1.02
B(8)	1.10	1.07
B(9)	1.10	1.07
B(10)	1.09	1.09
B(11)	1.06	1.10
B(12)	1.10	1.07

(a) Standard deviations calculated from least squares estimates of the errors in coordinates are $\pm 0.02 \text{ \AA}$ on all distances.

$\sigma = \pm 0.008 \text{ \AA}$ on distances involving only carbons and borons and $\sigma = \pm 0.04 \text{ \AA}$ on the distances between a hydrogen and the carbon or boron to which it is attached. These root mean square estimates of error based on the scatter are all larger than the errors calculated from the errors in coordinates estimated from the least squares refinements ($\sigma = \pm 0.002 \text{ \AA}$, $\pm 0.002 \text{ \AA}$, and $\pm 0.02 \text{ \AA}$, respectively) and it is the opinion of the authors that the r.m.s. errors are more realistic estimates of the actual errors in these interatomic distances. The intramolecular distances between the hydrogen atoms of Cage 1 and those of Cage 2 fall into four groups: 2.59 \AA for H(1) to H(1)' and to H(2)', for H(2) to H(1)' and H(4)', and for H(4) to H(2)'; 2.53 \AA for H(4) to H(7)' and for H(7) to H(4)'; 2.70 \AA for H(7) to H(8)' and for H(8) to H(7)'; and 2.62 \AA for H(8) to H(8)'. The unprimed and primed labels refer to atoms in Cage 1 and Cage 2, respectively. All standard deviations are $\pm 0.03 \text{ \AA}$.

Averages of various types of bond angles are given in Table VI. There are no surprises in the table since the angles differ, as expected, from the values of 60° and 108° for the angles in the triangular and pentagonal rings, respectively, of a regular icosahedron distorted by insertion of two carbons and a nickel atom into the cage.

The molecular packing is shown by the stereoscopic pair drawing of the unit cell shown in Figure 3. There are only six intermolecular hydrogen to hydrogen distances less than 2.60 \AA . These are H(11) - H(8)', 2.40 \AA ; H(10) - H(1)', 2.42 \AA ; H(1) - H(11)', 2.42 \AA ; H(2) - H(12), 2.49 \AA ; H(11) - H(5)', 2.54 \AA ; and H(12) - H(1)', 2.58 \AA , where the unprimed and the primed labels indicate atoms in Cage 1 and Cage 2, respectively. Because the center of gravity of the electron density

Table VI

Average Bond Angles^a

TYPE				
Atom 1	Atom 2	Atom 3	Number	Angle
Angles around all triangular faces				
C	Ni	C	2	45.7 ± 0.2
C	Ni	B	4	48.7 ± 0.3
B	Ni	B	4	51.6 ± 0.2
Ni	C	C	4	67.2 ± 0.3
Ni	C	B	4	66.4 ± 0.3
Ni	B	C	4	64.9 ± 0.1
Ni	B	B	8	64.2 ± 0.3
C	B	C	2	55.9 ± 0.2
C	C	B	4	62.1 ± 0.2
B	C	B	8	63.1 ± 0.2
C	B	B	16	58.4 ± 0.3
B	B	B	60	60.0 ± 0.1
Angles around all pentagonal rings				
Ni	C	B	8	124.8 ± 0.3
Ni	B	B	12	116.2 ± 0.4
C	Ni	B	8	83.9 ± 0.9
B	Ni	B	2	88.1 ± 0.4
C	C	B	8	112.1 ± 0.3
C	B	B	24	103.7 ± 0.2
B	B	B	42	108.5 ± 0.3
Angles involving hydrogen atoms attached to Atom 2				
Ni	C	H	4	105.4 ± 0.5

Table VI (continued)

Ni	B	H	6	114.3 ± 1.4
C	C	H	4	116.1 ± 0.7
B	C	H	12	118.9 ± 1.1
C	B	H	12	118.6 ± 0.4
B	B	H	72	122.6 ± 0.5

(a) The error given is the root mean square scatter, σ , of the \underline{n} individual values, \underline{a}_i , around the average, \bar{a} , where $\sigma = [\sum(\underline{a}_i - \bar{a})^2]^{1/2}/(\underline{n} - 1)$.

around a bonded hydrogen found in an X-ray analysis is not usually coincident with the position of the nucleus, a hydrogen appears to be too close to the atom to which it is bonded, thus making the intermolecular hydrogen distances appear to be too long. So although the distances appear to be too long for normal van der Waals contacts (2.40 Å), it is likely that they actually are shorter and that normal van der Waals interactions are holding the crystal together.

An indication of the asymmetry of the molecule is demonstrated by the molecular packing in the crystal lattice. The molecule shown in Figure 1 is the particular rotational isomer in which, looking from B(10) in one cage to the nickel, the opposite cage is staggered by a clockwise rotation of 36° from the position in which the carbons would be eclipsed. An equally probable isomer should and does result from a counterclockwise rotation from the eclipsed position. In a more symmetrical molecule, these two isomers might be sufficiently equivalent in shape that either isomer could pack in any given position in the crystal lattice. If this were the case, C(2) would appear to be equally disordered with B(4) in both cages. In this work, however, it is found that both isomers are present in the crystal and that they are sufficiently different that each must occupy its own position in the lattice. The two enantiomorphic rotational isomers are related to each other here by the c glide plane and the inversion center.

Acknowledgments

The authors wish to express thanks to Prof. M. Frederick Hawthorne and Mr. Leslie F. Warren, Jr., for supplying us with the crystals used in this work.

Figure Captions

- Figure 1: Skeletal drawing of $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$ showing the numbering system used (hydrogen atoms not shown).
- Figure 2: Stereoscopic pair drawing of a complete $\text{Ni}(\text{B}_9\text{C}_2\text{H}_{11})_2$ molecule. Thermal ellipsoid boundaries are at the 40% probability level. For this drawing the hydrogens were given artificial thermal parameters, $\underline{B} = 0.5$.
- Figure 3: Stereoscopic pair drawing of the unit cell (hydrogen atoms not shown). The origin is at the left rear corner of the unit cell. All thermal ellipsoids here are artificial. Nickel atoms are shown as the largest circles, medium size circles designate carbon atoms and boron atoms are shown by the smallest circles.

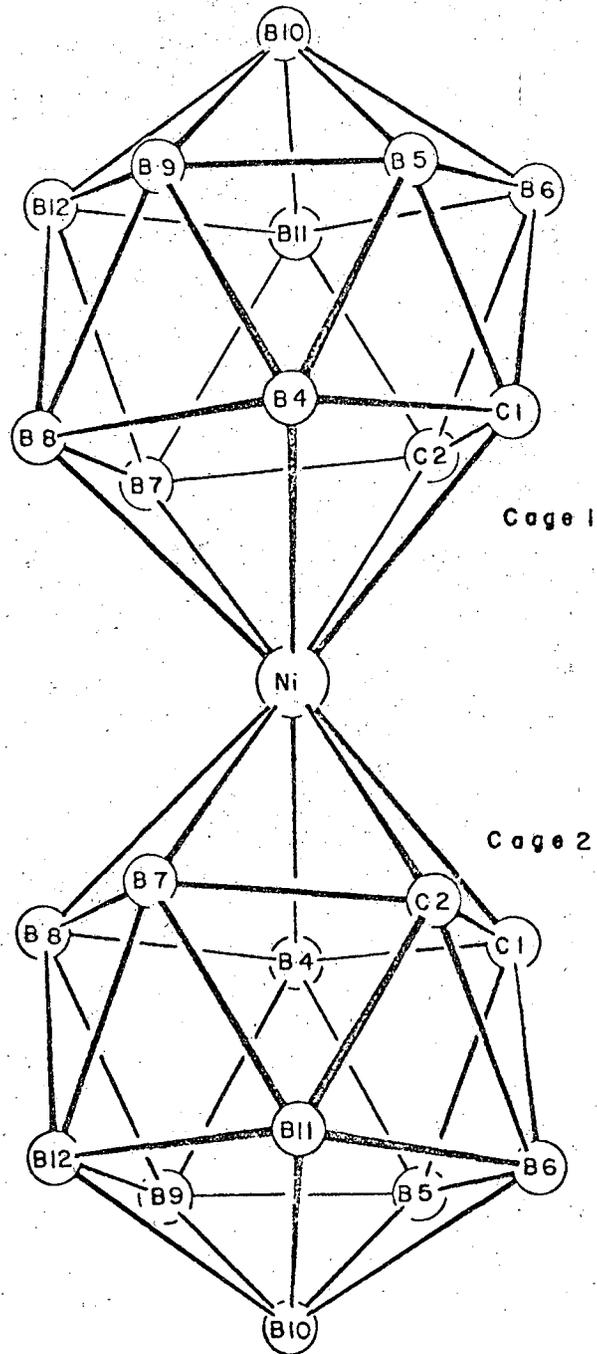
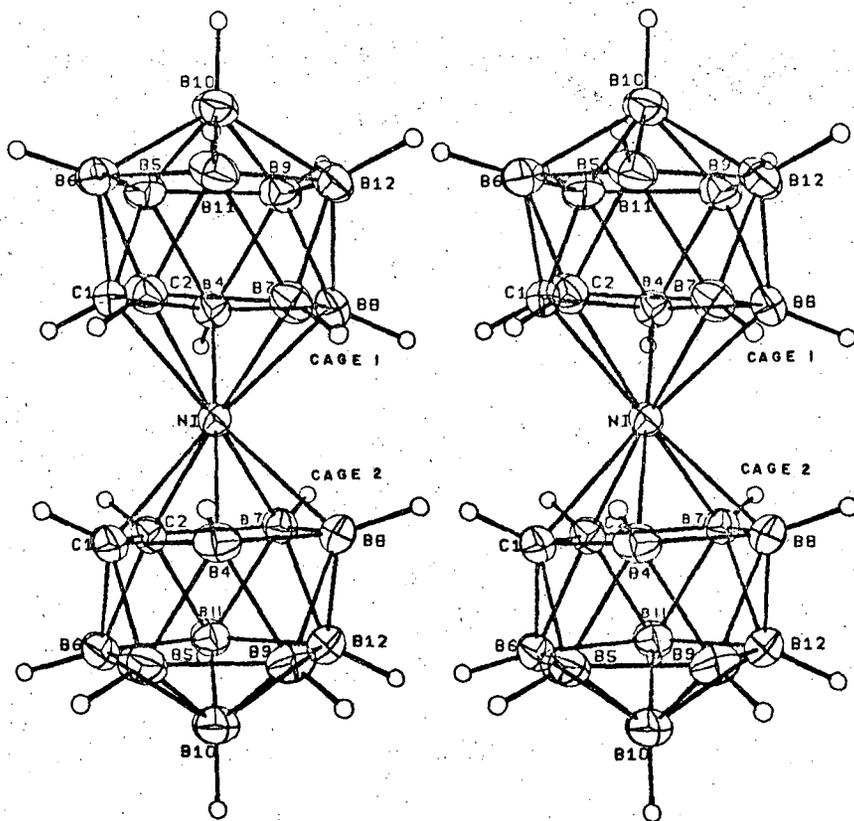


Figure 1



XPL 6811-6215

Figure 2

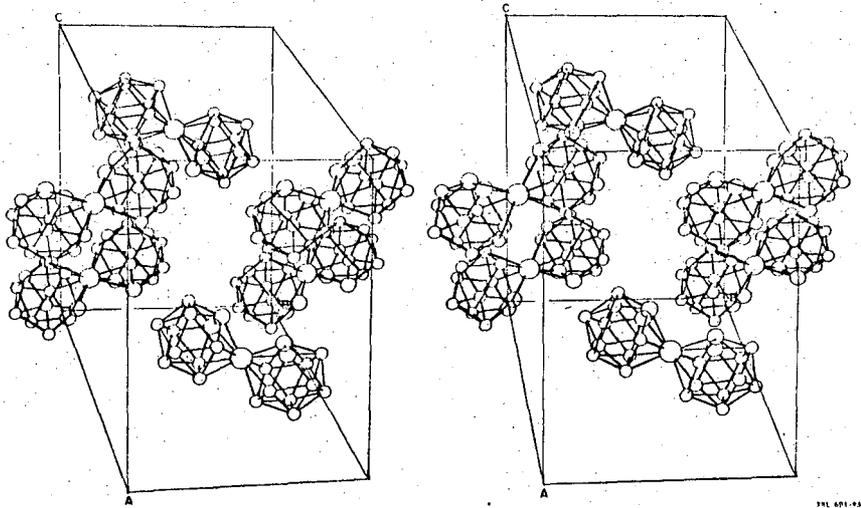


Figure 3

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