The Crystal Structure and Molecular Configuration of an Asymmetric 1,2-Dimethyl-1,2-dicarbollide Complex of Nickel, Racemic (3,4′)-[(CH$_3$)$_2$B$_9$C$_2$H$_9$]$_2$Ni^{IV}[1]

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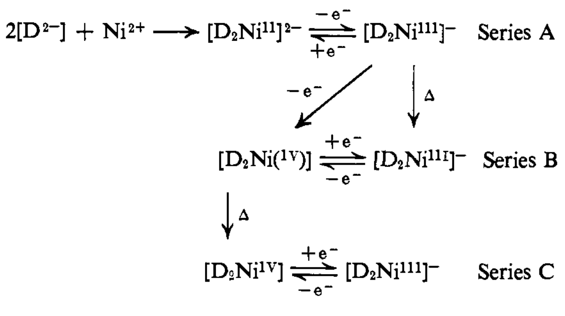
Abstract: [(CH$_3$)$_2$B$_9$C$_2$H$_9$]$_2$Ni^{IV} has previously been shown to exist in two modifications, one of which (isomer B) shows four types of methyl protons in its magnetic resonance spectrum and may be resolved into enantiomers *via* the corresponding {[(CH$_3$)$_2$B$_9$C$_2$H$_9$]$_2$Ni^{III}}$^-$ anion. An X-ray structural study of racemic isomer B shows it to be 3,4′-*commo*-[1,2-dimethyl-1,2-dicarba-3-nickela-*closo*-dodecaborane]-[1′,2′-dimethyl-1′,2′-dicarba-4′-nickela-*closo*-dodecaborane]. The complex crystallizes in the centrosymmetric monoclinic space group P2$_1$/n (C_{2h}^5; no. 14) with a = 13.489 ± 0.010, b = 20.223 ± 0.012, c = 7.626 ± 0.006 Å, β = 93.62 ± 0.05°, V = 2076 Å^3, Z = 4. Observed and calculated densities are 1.23 ± 0.05 and 1.215 g cm^{-3}, respectively. The use of three-dimensional counter data to sin θ = 0.75 (Cu Kα radiation) has led to the location of all nonhydrogen atoms, the final discrepancy index being R_F = 8.64% for the 1396 independent nonzero reflections. The discrete molecular units of [(CH$_3$)$_2$B$_9$C$_2$H$_9$]$_2$Ni^{IV} are separated by normal van der Waals distances. The Ni^{IV} ion is "sandwiched" between two mutually staggered 1,2-dimethyl-1,2-dicarbollide ligands and is the common (3,4′) apex of the two icosahedra. Thus, in one dicarbollide ligand, both C(1) and C(2) are in the basal pentagonal bonding face, whereas in the other ligand only C(1′) is directly bonded to the nickel, with C(2′) being in the upper pentagonal plane of this icosahedron. There is an angle of 14° 51′ between the bonding faces of the two dicarbollide ligands.

An unusual series of Ni(III) and Ni(IV) complexes of the 1,2-dimethyl-1,2-dicarbollide [D^{2-}] ligand has recently been prepared.[4] Chemical studies[4] show the following sequence of isomerization and redox reactions (Scheme I). There are three discrete Ni(III) derivatives and two Ni(IV) derivatives. The series B [D$_2$Ni^{III}]$^-$ ion has been resolved into enantiomers and oxidized to optically active series B [D$_2$Ni^{IV}]. The series B [D$_2$Ni^{IV}] exhibits four types of methyl protons in its proton magnetic resonance spectrum, whereas series C [D$_2$Ni^{IV}] shows only two kinds of methyl protons. The present structural study was undertaken in order to provide an unambiguous explanation for the optical activity and the four different methyl environments in series B [D$_2$Ni^{IV}].

Scheme I



Structural studies of related complexes in this series have been performed by other workers.[5,6]

Unit Cell and Space Group

Crystals of racemic series B [(CH$_3$)$_2$B$_9$C$_2$H$_9$]Ni^{IV} were supplied by Professor M. F. Hawthorne of the University of California, Riverside. Optical examination and a reciprocal lattice symmetry of C_{2h} (2/m) indicated that the crystals belonged to the monoclinic system. A survey of 0-2kl, hk0-2 Weissenberg photographs and h0-1l, 0-1kl precession photographs (all taken with Cu Kα radiation) revealed the systematic absences h0l for $h + l = 2n + 1$ and 0k0 for $k = 2n + 1$, consistent with the centrosymmetric space group P2$_1$/n (C_{2h}^5; no. 14).

Unit cell parameters, calculated from calibrated (a_{NaCl} = 5.640 Å) zero level precession photographs (Cu Kα radiation; $\bar{\lambda}$ 1.5418 Å) at 23 ± 2° are: a = 13.489 ± 0.010, b = 20.223 ± 0.012, c = 7.626 ± 0.006 Å, β = 93.62 ± 0.05°. (Errors given are the "maximum possible errors" based on the sum of the inaccuracies involved in measuring (on precession photographs) the positions of diffraction rows from the crystal under investigation, and from our standard NaCl crystal.) The unit cell volume is 2076 Å^3. The observed density of 1.23 ± 0.05 g cm^{-3} (by flotation in aqueous zinc iodide solution) agrees with that calculated for M = 379.81 and Z = 4 (ρ_{calcd} = 1.215 g cm^{-3}).

Collection and Reduction of X-Ray Diffraction Data

The complex crystallizes as bright orange platelets with well-developed (010) faces. Most of the supplied crystals appeared to be twinned and, of a total of some 40–50 examined by diffraction methods, only two were found to be suitable for a structural analysis. The crystals are air-stable and are not X-ray sensitive. Two crystals were used during the analysis. Crystal I (0.12 × 0.06 × 0.23 mm) was aligned along the c axis, and crystal II (0.14 × 0.09 × 0.26 mm) was aligned along the a axis. (Dimensions refer sequentially to $\vec{a}$, $\vec{b}$, $\vec{c}$.)

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[2] Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[3] National Institutes of Health Predoctoral Research Fellow.

[4] M. F. Hawthorne and L. F. Warren, Jr., personal communications; also L. F. Warren, Jr., and M. F. Hawthorne *J. Amer. Chem. Soc.*, 92, 1157 (1970).

[5] D. St. Clair, A. Zalkin, and D. H. Templeton, *ibid.*, 92, 1173 (1970).

[6] R. M. Wing, *ibid.*, 92, 1187 (1970).

Intensity data were collected with a 0.01°-incrementing Buerger automated diffractometer, using a "stationary background, ω-scan, stationary background" counting sequence. The apparatus and the experimental technique have been described previously.[7] Details specific to the present analysis include: (i) Cu Kα radiation ($\bar{\lambda}$ 1.5418 Å) was used. (ii) The scan angle was chosen as $\omega(hkl) = [3.00 + 1.0/\mathrm{L}(hkl)]°$, where $1/\mathrm{L}(hkl)$ is the Lorentz factor for the reflection hkl.[8] The count associated with this scan is $C(hkl)$. (iii) Initial and final backgrounds, $B_1(hkl)$ and $B_2(hkl)$, were each counted for one-fourth the time of the main scan. (iv) The overall stability of the system was monitored by remeasuring a carefully preselected check reflection after every 20 reflections. The maximum deviation from the mean was ~2.5%. (v) $I(hkl)$, the net intensity of the reflection hkl, was calculated as

$$I(hkl) = C(hkl) - 2[B_1(hkl) + B_2(hkl)]$$

Reflections were weighted according to the scheme

$$I(hkl) > 4900,\ \sigma\{I(hkl)\} = 0.1[I(hkl)]$$

$$I(hkl) \leqslant 4900,\ \sigma\{I(hkl)\} = 7.0[I(hkl)]^{1/2}$$

Data were subsequently rejected on two bases: (i) $B_1(hkl)/B_2(hkl)$ or $B_2(hkl)/B_1(hkl) \geqslant 4.0$, symptomatic of overlap of adjacent reflections. (ii) $I(hkl) \leqslant 3[C(hkl) + B_1(hkl) + B_2(hkl)]^{1/2}$, indicating that the reflection was not significantly different from zero.

With crystal I mounted along the c axis, equiinclination geometry was used in collecting a total of 2275 reflections in the zones hk0–6. A total of 2144 reflections from the zones 0–11kl were collected from crystal II. This represents data complete to $\sin\theta = 0.75$ and includes all data visible on long-exposure Weissenberg films All data were corrected for Lorentz and polarization effects, and absorption corrections were applied.[9] Transmission factors varied from 0.88 to 0.94 for data from crystal I (volume = 0.0012 mm^3) and from 0.77 to 0.90 for data from crystal II (volume = 0.0033 mm^3). All data were placed on a common scale *via* a least-squares procedure which minimizes a sum of residuals linear in the logarithms of the individual scale factors.[10] The resulting 1396 independent nonzero reflections were placed on an absolute scale by means of a Wilson plot,[11] which also yielded the overall isotropic thermal parameter $\bar{B}$ = 3.14 Å^2.

All subsequent calculations were preformed using the CRYRM system.[12]

Solution and Refinement of the Structure

Throughout the analysis scattering factors for *neutral* carbon, boron, and hydrogen were used;[13a] the Thomas–Fermi–Dirac values for neutral nickel[13b] were corrected for the real, but not for the imaginary, component of dispersion ($\Delta f'$(Ni) = −3.1 e, $\Delta f''$(Ni) = +0.6 e).[13c] The residual minimized during least-squares refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$. Discrepancy indices are defined thus

$$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_{wF^2} = \Sigma_w(|F_o|^2 - |F_c|^2)^2/\Sigma_w|F_o|^4$$

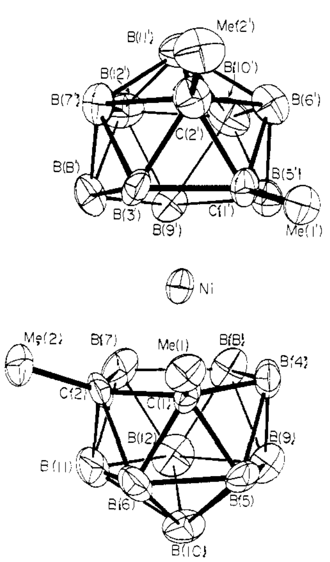

Figure 1. The (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ molecule, projected on (100). The 68% probability envelopes of the thermal vibration ellipsoids are shown. (The diagram was constructed using OTLIPS, an IBM 1620/CALCOMP program by Dr. P. H. Bird.)

The position of the nickel atom (x = 0.683, y = 0.263, z = 0.488) was determined from a three-dimensional Patterson synthesis. A three-dimensional Fourier synthesis phased only by the nickel atom (R_F = 44.3%) yielded unambiguously the positions of all nonhydrogen atoms. One cycle of least-squares refinement of positional and individual isotropic thermal parameters led to a reduction in the discrepancy indices to R_F = 22.11% and R_{wF^2} = 33.85%. Three cycles of full-matrix least-squares refinement of all positional parameters, isotropic thermal parameters for boron and carbon atoms, and anisotropic thermal parameters for the nickel atom led to convergence at R_F = 13.00%, R_{wF^2} = 2.75%. A three-dimensional difference Fourier synthesis now showed clear evidence for anisotropic motion for boron and carbon atoms, and also led to the location of all hydrogen atoms other than those of the methyl groups. (Peak heights, in e Å^{-3}, were: H(4), 0.55; H(5), 0.44; H(6), 0.44; H(7), 0.30; H(8), 0.44; H(9), 0.38; H(10), 0.35; H(11), 0.34; H(12), 0.36; H(3′), 0.42; H(5′), 0.42; H(6′), 0.45; H(7′), 0.55; H(8′), 0.46; H(9′), 0.37; H(10′), 0.26; H(11′), 0.43; H(12′), 0.34. These may be compared with carbon atom peak heights of ~3.5 e Å^{-3} on an "observed" Fourier synthesis at this stage.) Refinement was continued using anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms (other than those of the methyl groups) were included in calculated positions with d(B–H) = 1.00 Å and the appropriate icosahedral geometry.[14]

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[7] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 7, 1123 (1968).

[8] The term 1.0/L(hkl) allows for the extension of low-order reflections on upper level data; see D. C. Phillips, *Acta Crystallogr.*, 7, 746 (1954).

[9] Absorption corrections were applied using GNABS, a general absorption-correction program for the IBM 7094: see C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

[10] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

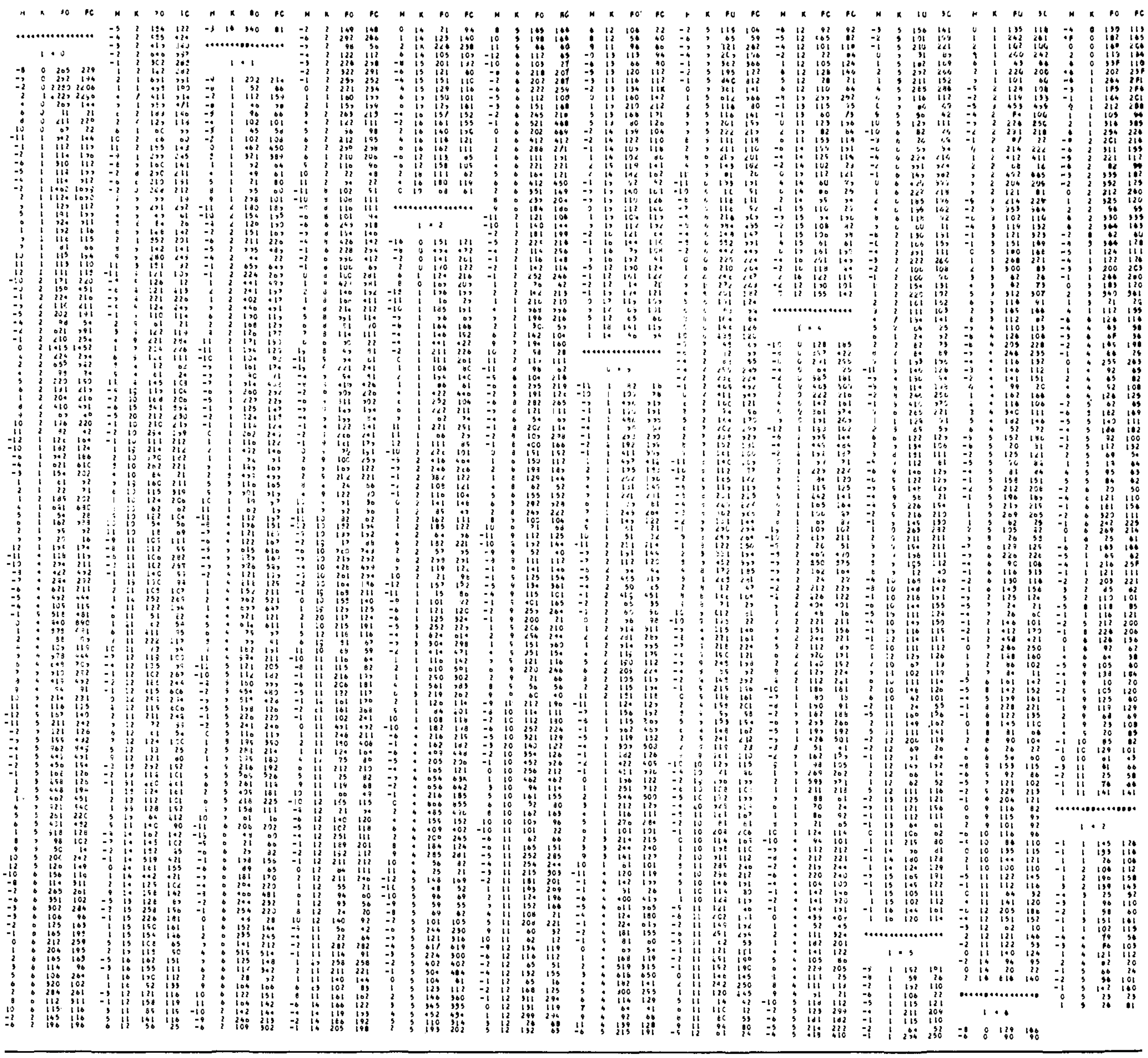
[11] A. J. C. Wilson, *Nature*, **150**, 152 (1942).

[12] CRYRM is an integrated sequence of crystallographic routines for the IBM 7094 computer, compiled under the direction of Professor R. E. Marsh at the California Institute of Technology.

[13] "International Tables for X-Ray Crystallography, Volume 3," The Kynoch Press, Birmingham, England, 1962: (a) pp 202–203; (b) p 210; (c) p 214.

[14] The calculated positions are all close to the center of the hydrogen peaks observed on the 13.00% difference Fourier synthesis.

Table I. Observed and Calculated Structure Factors for (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ [a]



[a] The table shows h, k, $10|F_o|$, $10|F_c|$ in blocks of constant l.

Each was assigned an isotropic thermal parameter of 1.4 Å^2. Neither the positions nor the thermal parameters of the hydrogen atoms were allowed to refine. Hydrogen atom positions were, however, redefined with respect to the new boron positions after each cycle of refinement. Seven cycles of "two-matrix"[15] refinement of positional and anisotropic thermal parameters for the 27 nonhydrogen atoms led to convergence at R_F = 8.64% and R_{Fw^2} = 2.12%; in the last cycle, no parameter varied by more than one-tenth of its standard deviation and refinement was judged to be complete. A final difference Fourier synthesis showed no unexpected features (nor any methyl hydrogens), thus validating the results of the least-squares refinement procedure, and confirming the correctness of the molecular structure. The final standard deviation of an observation of unit weight was 1.35.

Table I shows the final observed and calculated structure factors. Atomic coordinates are collected in Table II. Anisotropic thermal parameters are listed in Table III; their associated atomic vibration ellipsoids are defined in Table IV and illustrated in Figure 1.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table V(a). Average bond distances, with their root-mean-square deviations from the mean, are collected in Table V(b). Average bond angles are given in Table VI. (Since the linked icosahedral $(B_9C_2)_2Ni$ skeleton of the molecule defines 240 bond angles, and the methyl carbon atoms give rise to 20 more angles (neglecting all hydrogen atoms) it was thought inappropriate to report *individual* bond angles.) Figure 1 shows the molecule projected

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[15] Due to a limitation of 32K in the storage space of the IBM 7094, refinement had to be carried out using two submatrices. Matrix 1 contained the scale factor and all parameters for Ni, C(1), C(2), Me(1), Me(2), and B(4)–B(12); matrix 2 contained all parameters for C(1′) C(2′), Me(1′), Me(2′), B(3′), and B(5′)–B(12′).

Table II. Final Atomic Positions[a] for (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$

Atom	x	y	z
Ni	0.68404 (10)	0.26578 (9)	0.48961 (17)
C(1)	0.7806 (7)	0.1791 (5)	0.4434 (11)
C(2)	0.7256 (7)	0.1737 (5)	0.6281 (12)
C(1′)	0.7536 (7)	0.3524 (5)	0.3846 (11)
C(2′)	0.7709 (8)	0.4196 (6)	0.5207 (16)
Me(1)	0.8931 (7)	0.1963 (6)	0.4534 (13)
Me(2)	0.7855 (8)	0.1845 (6)	0.8055 (12)
Me(1′)	0.8356 (8)	0.3446 (6)	0.2598 (13)
Me(2′)	0.8728 (8)	0.4577 (7)	0.5203 (17)
B(4)	0.6963 (10)	0.2008 (7)	0.2785 (15)
B(5)	0.7378 (9)	0.1196 (7)	0.3031 (15)
B(6)	0.7551 (10)	0.1026 (7)	0.5263 (18)
B(7)	0.5997 (10)	0.1928 (8)	0.5927 (16)
B(8)	0.5755 (9)	0.2046 (7)	0.3632 (18)
B(9)	0.6136 (9)	0.1331 (7)	0.2571 (17)
B(10)	0.6470 (9)	0.0735 (7)	0.4123 (19)
B(11)	0.6461 (12)	0.1111 (8)	0.6207 (18)
B(12)	0.5533 (10)	0.1292 (8)	0.4543 (21)
B(3′)	0.7760 (9)	0.3409 (7)	0.6129 (14)
B(5′)	0.6292 (8)	0.3463 (7)	0.3353 (15)
B(6′)	0.6851 (8)	0.4223 (7)	0.3537 (16)
B(7′)	0.7222 (9)	0.4043 (7)	0.7166 (16)
B(8′)	0.6581 (8)	0.3296 (7)	0.7073 (15)
B(9′)	0.5667 (8)	0.3309 (7)	0.5371 (15)
B(10′)	0.5744 (9)	0.4079 (7)	0.4371 (20)
B(11′)	0.6612 (10)	0.4565 (7)	0.5588 (20)
B(12′)	0.5937 (9)	0.4018 (7)	0.6650 (20)
H(4)	0.7116	0.2282	0.1743
H(5)	0.7793	0.0976	0.2161
H(6)	0.5220	0.2349	0.3146
H(7)	0.5581	0.2148	0.6798
H(8)	0.8086	0.0723	0.5748
H(9)	0.5790	0.1206	0.1422
H(10)	0.6377	0.0249	0.3928
H(11)	0.6308	0.0838	0.7249
H(12)	0.4830	0.1138	0.4577
H(3′)	0.8380	0.3203	0.6670
H(5′)	0.6011	0.3288	0.2200
H(6′)	0.6932	0.4502	0.2473
H(7′)	0.7503	0.4218	0.8319
H(8′)	0.6500	0.3018	0.8138
H(9′)	0.5047	0.3040	0.5421
H(10′)	0.5124	0.4286	0.3831
H(11′)	0.6554	0.5053	0.5765
H(12′)	0.5451	0.4168	0.7504

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the preceding number.

on (100) and illustrates the scheme used for numbering all nonhydrogen atoms. The hydrogen atoms of the icosahedra, which have been omitted from the diagram for the sake of clarity, are numbered similarly to their attached boron atoms.

The d^6 Ni(IV) ion is "sandwiched" between two mutually staggered carborane moieties and achieves the 18 outer electron ("noble gas") configuration, compatible with the observed diamagnetism of the complex, by the donation of six electrons from each of the substituted dicarbollide ligands.

In each dicarbollide ligand the two carbon atoms of the icosahedral framework remain adjacent to each other and retain their bonded methyl groups, as in the parent $[(CH_3)_2B_9C_2H_9{}^{2-}]$ dianion. However, the ligands have different configurations. The lower ligand (unprimed in Figure 1) has its two icosahedral carbon atoms in the bonding pentagonal face: this ligand may thus be described as a (3)-1,2-dimethyl-1,2-dicarbollide dianion. The upper ligand (primed in Figure 1) has only one carbon atom in the basal pentagonal face; the second icosahedral carbon of this ligand does *not* bond directly to the nickel ion. This ligand is thus a (4)-1,2-dimethyl-1,2-dicarbollide dianion. The molecule thus may be systematically named as 3,4′-*commo*-[1,2-dimethyl-1,2-dicarba-3-nickela-*closo*-dodecaborane]-[1′,2′-dimethyl-1′,2′-dicarba-4′-nickela-*closo*-dodecaborane].[16]

It should be emphasized that the present (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ molecule is the first reported example of a transition metal complex in which a dicarbollide ligand fails to have both carbon atoms in the basal (bonding) pentagonal face. In all transition metal dicarbollide complexes for which structural studies have previously been published (*viz.*, $(C_5H_5)Fe(B_9C_2H_{11})$,[17] $Cs^+[(B_9C_2H_{11})Re(CO)_3{}^-]$,[18] $[Et_4N^+]_2[Cu(B_9C_2H_{11})_2{}^{2-}]$,[19] $Cs^+[Co(B_9C_2H_{11})_2{}^-]$,[20] $[PPh_3Me^+][Cu(B_9C_2H_{11})_2{}^-]$,[21] $[Me_4N^+][Co(B_9C_2H_8Br_3)_2{}^-]$,[22] and $(B_9C_2H_{10})_2CoS_2CH$[23]), the carborane moiety is present as a (3)-1,2-dicarbollide ligand. The present (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ molecule also represents the first reported example of a bis(dicarbollide) complex in which the two dicarbollide ligands are found to bond differently to the central metal ion. Thus, the $[Co(B_9C_2H_8Br_3)_2{}^-]$ ion has an inversion center at the metal atom,[22] the $[Co(B_9C_2H_{11})_2{}^-]$ ion is disordered such that the relative orientation of the ligands cannot properly be determined,[20] the $(B_9C_2H_{10})_2CoS_2CH$ molecule has C_2 symmetry with the pairs of dicarbollide carbons lying in close proximity,[23] and the $[Cu(B_9C_2H_{11})_2{}^-]$[21] and $[Cu(B_9C_2H_{11})_2{}^{2-}]$[19] ions retain C_{2h} symmetry even though their dicarbollide cages are "slipped" relative to each other; and these compounds may be regarded formally as pseudo-π-allyl complexes with only the B_3 fragment of the basal B_3C_2 moiety bonding to the central copper ions.

In the (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ molecule the bonding pentagonal faces of the carborane ligands (hereafter called α and α') therefore contain the atoms C(1)–C(2)–B(7)–B(8)–B(4) and C(1′)–B(3′)–B(8′)–B(9′)–B(5′), respectively. The β and β' pentagons, which lie directly above and in a staggered conformation with respect to α and α', are defined by B(5)–B(6)–B(11)–B(12)–B(9) and C(2′)–B(7′)–B(12′)–B(10′)–B(6′), respectively. As shown in Table VII, the five atoms of the α pentagon have a root-mean-square (rms) deviation of 0.035 Å from the least-squares plane[24] $0.1599X + 0.9733Y + 0.1641Z = 5.7466$, and the atoms of the β pentagon have an rms deviation of 0.020 Å from the least-squares plane[24] $0.1538X + 0.9760Y + 0.1537Z = 4.2000$. The dihedral angle between the α and β planes is 1° 24′ (*i.e.*, not significantly different from zero). In the other ligand, the α' pentagon has an rms deviation of 0.012 Å from the plane[24] $-0.0995X + 0.9866Y + 0.1291Z = 6.4089$, and the β' pentagon has an rms deviation of 0.030 Å from the plane[24] $-0.1201X + 0.9871Y + 0.1239Z = 7.8311$.

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(24) Cartesian coordinates, see Table VII.

Table III. Anisotropic Thermal Parameters[a,b] for (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$

Atom	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
Ni	62.3 (1.1)	40.7 (0.6)	165.9 (3.2)	6.5 (1.4)	60.9 (2.5)	−10.0 (2.5)
C(1)	102 (9)	45 (5)	148 (19)	31 (10)	50 (19)	−28 (16)
C(2)	112 (9)	36 (4)	166 (22)	14 (10)	79 (24)	69 (15)
C(1′)	75 (7)	49 (4)	175 (21)	19 (9)	77 (20)	73 (15)
C(2′)	98 (9)	57 (5)	339 (32)	11 (12)	84 (30)	22 (21)
Me(1)	69 (7)	49 (5)	354 (27)	30 (10)	51 (23)	−44 (19)
Me(2)	153 (11)	57 (5)	177 (24)	19 (12)	−89 (26)	14 (18)
Me(1′)	93 (7)	52 (5)	297 (27)	9 (10)	200 (25)	−1 (18)
Me(2′)	85 (8)	71 (6)	605 (42)	−55 (12)	61 (32)	−14 (28)
B(4)	111 (11)	47 (6)	156 (24)	−11 (14)	−18 (27)	20 (19)
B(5)	102 (10)	35 (5)	241 (29)	47 (11)	47 (27)	−56 (18)
B(6)	122 (11)	37 (5)	289 (34)	48 (12)	98 (31)	76 (21)
B(7)	106 (11)	58 (6)	280 (28)	20 (14)	197 (29)	−77 (23)
B(8)	71 (9)	57 (6)	288 (29)	22 (12)	−2 (25)	−55 (23)
B(9)	87 (10)	56 (6)	284 (34)	−7 (13)	9 (31)	−64 (24)
B(10)	90 (9)	38 (5)	396 (36)	−35 (12)	105 (32)	−41 (24)
B(11)	169 (15)	47 (6)	267 (35)	41 (17)	278 (40)	55 (23)
B(12)	81 (9)	60 (7)	393 (43)	−35 (14)	65 (34)	−24 (29)
B(3′)	101 (10)	46 (5)	170 (26)	27 (12)	−53 (26)	−49 (19)
B(5′)	77 (9)	45 (5)	233 (28)	44 (11)	8 (26)	174 (19)
B(6′)	75 (9)	49 (6)	335 (36)	−12 (12)	19 (29)	54 (23)
B(7′)	90 (9)	58 (6)	227 (28)	−1 (13)	43 (27)	4 (21)
B(8′)	76 (8)	53 (6)	256 (28)	15 (12)	168 (26)	72 (20)
B(9′)	70 (8)	44 (5)	266 (28)	−16 (11)	42 (25)	−37 (20)
B(10′)	77 (9)	46 (6)	423 (42)	35 (13)	−48 (32)	57 (25)
B(11′)	92 (10)	40 (5)	435 (42)	23 (13)	131 (35)	−44 (26)
B(12′)	96 (10)	41 (5)	426 (43)	1 (13)	187 (34)	−45 (24)

[a] See footnote *a*, Table II. [b] The anisotropic thermal parameter, T, is defined as: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table IV. Direction Cosines for the Atomic Vibration Ellipsoids in (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$[a-c]

Atom	B_{max} (dc's, major axis)	B_{med} (dc's, median axis)	B_{min} (dc's minor axis)
Ni	6.73 (−133, −989, 60)	5.17 (778, −67, 624)	3.03 (−614, 130, 779)
C(1)	9.07 (−694, −720, 11)	6.12 (660, −630, 409)	2.93 (−288, 291, 913)
C(2)	9.01 (805, 438, 401)	6.30 (−573, 748, 335)	2.38 (−153, −499, 853)
C(1′)	8.43 (370, 915, 160)	5.71 (739, −394, 547)	3.20 (−564, 84, 822)
C(2′)	9.97 (336, 817, 469)	8.16 (441, −577, 688)	6.12 (−832, 24, 554)
Me(1)	9.70 (−200, −741, 641)	7.67 (465, 504, 728)	3.91 (−862, 444, 244)
Me(2)	12.23 (−927, −302, 223)	9.17 (−263, 946, 188)	3.50 (268, −116, 956)
Me(1′)	10.38 (673, 158, 722)	8.49 (56, −985, 163)	2.90 (−737, 69, 672)
Me(2′)	14.34 (150, −300, 942)	12.65 (−371, 866, 335)	4.79 (−917, −400, 18)
B(4)	8.77 (−781, 602, 166)	7.28 (−614, −788, −33)	3.51 (111, −128, 986)
B(5)	9.37 (−760, −628, 168)	6.59 (441, −308, 843)	2.64 (−478, 714, 511)
B(6)	11.61 (702, 523, 483)	6.07 (−667, 246, 704)	3.83 (249, −816, 521)
B(7)	11.15 (405, −641, 652)	9.84 (679, 689, 255)	2.28 (−613, 339, 713)
B(8)	10.57 (−244, −874, 420)	5.92 (124, 402, 907)	4.80 (−962, 273, 10)
B(9)	10.23 (28, −875, 483)	6.45 (−936, 146, 319)	5.41 (350, 461, 815)
B(10)	10.79 (450, −403, 797)	6.61 (−530, 598, 602)	4.46 (−719, −693, 55)
B(11)	15.81 (804, 316, 504)	6.82 (311, −945, 97)	2.93 (−507, −79, 858)
B(12)	11.05 (355, −809, 468)	8.74 (−74, 475, 877)	4.97 (−932, −346, 109)
B(3′)	9.75 (−654, −680, 332)	5.96 (−729, 684, −35)	3.27 (203, 265, 943)
B(5′)	9.00 (567, 818, 95)	5.54 (−274, 79, 958)	3.77 (777, −569, 269)
B(6′)	9.73 (−145, 735, 662)	6.44 (358, −585, 728)	5.20 (−922, −343, 179)
B(7′)	9.47 (−6, 999, 32)	6.70 (929, −6, 371)	5.09 (−371, −32, 928)
B(8′)	10.84 (398, 712, 579)	6.62 (584, −683, 439)	2.29 (−708, −163, 687)
B(9′)	8.19 (278, −800, 532)	5.46 (−72, 535, 842)	4.73 (−958, −272, 91)
B(10′)	10.93 (−150, 391, 908)	8.50 (−623, −751, 220)	3.80 (768, −532, 356)
B(11′)	11.21 (349, −166, 922)	7.75 (−620, −779, 94)	4.15 (−702, 605, 375)
B(12′)	12.14 (483, −205, 851)	6.80 (−412, −911, 14)	4.27 (−773, 357, 525)

[a] Direction cosines (dc's) are referred to the monoclinic axes. They have been multiplied by 10^3. [b] The major, median, and minor axes of the atomic vibration ellipsoids are defined in terms of B (the normal isotropic thermal parameter, having units of Å^2). The transformation to root-mean-square displacement, $(\bar{U}^2)^{1/2}$, is: $(\bar{U}^2)^{1/2} = [B/8\pi^2]^{1/2}$. [c] The 68% probability contours of the vibration ellipsoids are illustrated in Figure 1.

The dihedral angle between the α' and β' planes is 0° 00′. In none of these four systems does any atom deviate from its least-squares plane by more than 3σ, so each of the latitudinal pentagons is planar within experimental error.

There is a dihedral angle of 14° 51′ between the α and α' pentagonal planes, showing that the two 1,2-dimethyl-1,2-dicarbollide ligands are distinctly nonparallel. This is in contrast to other reported metallobis(carbollide) structures, in which the two dicarbollide

Table V(a). Interatomic Distances within the (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ Molecule[a]

Atoms	Distance, Å	Atoms	Distance, Å
Distances from nickel atom			
Ni–C(1)	2.225 (9)	Ni–B(7)	2.050 (13)
Ni–C(2)	2.195 (9)	Ni–B(8)	2.104 (13)
Ni–C(1′)	2.163 (9)	Ni–B(3′)	2.141 (12)
Ni...Me(1)	3.177 (10)	Ni–B(5′)	2.115 (12)
Ni...Me(2)	3.156 (11)	Ni–B(8′)	2.149 (12)
Ni...Me(1′)	3.200 (10)	Ni–B(9′)	2.107 (12)
Ni–B(4)	2.092 (13)		
Carbon–methyl distances			
C(1)–Me(1)	1.553 (14)	C(1′)–Me(1′)	1.511 (14)
C(2)–Me(2)	1.547 (14)	C(2′)–Me(2′)	1.577 (17)
Carbon–carbon distances			
C(1)–C(2)	1.636 (13)	C(1′)–C(2′)	1.717 (15)
Carbon–boron distances			
C(1)–B(4)	1.698 (16)	C(1′)–B(5′)	1.700 (15)
C(1)–B(5)	1.687 (15)	C(1′)–B(6′)	1.697 (16)
C(1)–B(6)	1.713 (16)	C(2′)–B(3′)	1.738 (17)
C(2)–B(6)	1.693 (16)	C(2′)–B(6′)	1.666 (17)
C(2)–B(7)	1.746 (16)	C(2′)–B(7′)	1.697 (17)
C(2)–B(11)	1.658 (17)	C(2′)–B(11′)	1.697 (18)
C(1′)–B(3′)	1.763 (15)		
Boron–boron bond lengths			
B(4)–B(5)	1.741 (17)	B(3′)–B(7′)	1.693 (17)
B(4)–B(8)	1.792 (18)	B(3′)–B(8′)	1.801 (17)
B(4)–B(9)	1.767 (18)	B(5′)–B(6′)	1.712 (17)
B(5)–B(6)	1.737 (18)	B(5′)–B(9′)	1.827 (17)
B(5)–B(9)	1.711 (18)	B(5′)–B(10′)	1.665 (18)
B(5)–B(10)	1.786 (18)	B(6′)–B(10′)	1.683 (19)
B(6)–B(10)	1.752 (19)	B(6′)–B(11′)	1.757 (19)
B(6)–B(11)	1.686 (20)	B(7′)–B(8′)	1.738 (17)
B(7)–B(8)	1.776 (19)	B(7′)–B(11′)	1.764 (19)
B(7)–B(11)	1.774 (20)	B(7)′–B(12′)	1.752 (18)
B(7)–B(12)	1.754 (20)	B(8′)–B(9′)	1.733 (17)
B(8)–B(9)	1.749 (19)	B(8′)–B(12′)	1.716 (18)
B(8)–B(12)	1.709 (20)	B(9′)–B(10′)	1.740 (18)
B(9)–B(10)	1.729 (19)	B(9′)–B(12′)	1.759 (18)
B(9)–B(12)	1.756 (20)	B(10′)–B(11′)	1.749 (20)
B(10)–B(11)	1.762 (20)	B(10′)–B(12′)	1.745 (19)
B(10)–B(12)	1.738 (20)	B(11′)–B(12′)	1.674 (20)
B(11)–B(12)	1.763 (31)		
Interannular contacts			
C(1)···C(1′)	3.559 (13)	B(7)···B(9′)	2.855 (18)
C(1)···B(3′)	3.523 (15)	B(8)···B(9′)	2.887 (17)
C(2)···B(3′)	3.452 (15)	B(8)···B(5′)	2.968 (17)
C(2)···B(8′)	3.348 (18)	B(4)···B(5′)	3.117 (17)
B(7)···B(8′)	2.994 (16)	B(4)···C(1′)	3.251 (16)
Methyl···methyl contacts (≤3.5 Å)			
Me(1)···Me(2)	3.152 (17)	Me(1′)···Me(2′)	3.056 (17)
Me(1)···Me(1′)	3.414 (17)		

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit of the previous number.

Table V(b). Average Bond Lengths in the (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ Molecule

Atoms	Number	Range[a]	Average[b]
Ni–C	3	2.163 (9)–2.225 (9)	2.194 (31)
Ni–B	7	2.050 (13)–2.149 (12)	2.109 (33)
C–C	2	1.636 (13)–1.717 (15)	1.677 (57)
C–B	13	1.658 (17)–1.763 (15)	1.704 (30)
B–B	35/60	1.665 (18)–1.827 (17)	1.742 (36)
C–Me	4	1.511 (14)–1.577 (17)	1.547 (28)

[a] Esd's for individual shortest and longest bonds are those obtained from the least-squares process *via* the matrix inverse to the normal equation matrix. [b] Esd's from "equivalent" bond lengths were calculated from the equation

$$\sigma^2 = \left\{\left[\sum_{i=1}^{i=N}(\chi_i-\bar{\chi})^2\right]\Big/(N-1)\right\}$$

where χ_i is the ith bond length and $\bar{\chi}$ is the mean of the N equivalent bond lengths.

Table VI. Average Bond Angles in the (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ Molecule

Atoms	No. of angles	Range (°)[a]	Average[b]
I. Angles around all triangular faces			
C–Ni–C	1	43.5 (0.4)	43.5
C–Ni–B	4	46.2 (0.4)–48.4 (0.5)	47.5 (1.1)
B–Ni–B	5	48.0 (0.5)–51.3 (0.5)	50.0 (1.3)
Ni–C–C	2	67.3 (0.5)–69.3 (0.5)	68.3 (1.4)
Ni–C–B	4	61.5 (0.5)–65.2 (0.5)	63.7 (1.8)
Ni–B–C	4	66.5 (0.5)–71.0 (0.6)	68.9 (2.0)
Ni–B–B	10	63.1 (0.6)–67.3 (0.6)	65.0 (1.2)
C–B–C	3	57.4 (0.6)–61.4 (0.7)	59.2 (2.1)
C–C–B	6	58.5 (0.7)–61.9 (0.7)	60.4 (1.3)
B–C–B	8	59.0 (0.7)–63.0 (0.8)	61.5 (1.4)
C–B–B	16	56.2 (0.7)–61.7 (0.7)	59.3 (1.4)
B–B–B	57/120	55.6 (0.7)–64.9 (0.8)	60.0 (1.7)
II. Angles around all pentagonal rings			
C–Ni–B	6	80.7 (0.5)–84.7 (0.5)	82.2 (2.2)
B–Ni–B	4	82.6 (0.5)–85.2 (0.5)	84.1 (1.1)
Ni–C–C	1	117.5 (0.6)	117.5
Ni–C–B	5	118.7 (0.7)–124.0 (0.7)	120.4 (2.3)
Ni–B–C	1	117.7 (0.7)	117.7
Ni–B–B	13	114.7 (0.8)–123.3 (0.8)	118.8 (2.1)
C–C–B	7	106.6 (0.8)–111.4 (0.9)	109.7 (1.5)
B–C–B	7	107.7 (0.8)–112.9 (0.9)	110.4 (1.9)
C–B–B	25	102.9 (1.0)–109.9 (0.9)	107.0 (1.8)
B–B–B	51/120	103.6 (0.9)–113.5 (1.0)	108.1 (2.2)
III. Angles involving methyl substituents			
Me–C–Ni	3	113.0 (0.6)–120.1 (0.7)	115.8 (3.7)
Me–C–C	4	112.6 (0.8)–120.2 (0.8)	117.2 (3.2)
Me–C–B	13/20	113.3 (0.8)–127.2 (0.8)	119.7 (4.7)

[a] Esd's for the individual lowest and highest values for a given type of bond angle are those obtained from the least-squares refinement. [b] Esd's for the average bond angles were calculated from the equation given in footnote *b* of Table V(b).

ligands are essentially parallel. However, there is a small dihedral angle (~3°) between the dicarbollide ligands in the $[Co(B_9C_2H_8Br_3)_2^-]$ ion, believed[22] to be due to interligand bromine···hydrogen repulsions. The dihedral angle of 14° 51′ in the present complex is also probably the result of steric, rather than electronic, effects. Pauling[25] estimates the van der Waals radius of a methyl group as 2.0 Å. The Me(1)···Me(1′) distance of 3.414 ± 0.017 Å in (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ is thus *ca.* 0.6 Å *below* the sum of the covalent radii, and presumably is the cause of the large separation of C(1) and C(1′) (3.559 ± 0.013 Å) as compared to the relatively short B(7)···B(9′) distance of 2.855 ± 0.018 Å directly opposite to this. (For other interannular contacts, see Table Va.)

It should be noted, however, that the observation of four distinct methyl resonances in the proton magnetic resonance spectrum[4] is the result of the four different chemical environments of methyl groups. There is no interlocking of methyl groups, as may easily be recognized by observing that C(1′), although as close as possible to C(1), is well removed from the vicinity of C(2).

The nickel ion lies 1.540 Å above the α plane and 1.518 Å below the α′ plane. Distances from the nickel to atoms of the α′ plane are essentially equal, the short-

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(25) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 261.

Table VII. Important Planes[a,b] in the (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ Molecule

Atom	Dev, Å	Atom	Dev, Å
α Plane: C(1), C(2), B(4), B(7), B(8) $+0.1599X + 0.9733Y + 0.1641Z = +5.7446$			
C(1)	−0.013 (10)	B(8)	−0.048 (14)
C(2)	−0.020 (10)	Ni	+1.540 (3)
B(4)	+0.039 (13)	Me(1)	+0.580 (10)
B(7)	+0.042 (14)	Me(2)	+0.530 (11)
β Plane: B(5), B(6), B(9), B(11), B(12) $+0.1538X + 0.9760Y + 0.1537Z = +4.2000$			
B(5)	+0.026 (12)	B(11)	+0.017 (15)
B(6)	−0.027 (14)	B(12)	−0.001 (15)
B(9)	−0.015 (13)	B(10)	−0.953 (14)
α′ Plane: C(1′), B(3′), B(5′), B(8′), B(9′) $-0.0995X + 0.9866Y + 0.1291Z = +6.4089$			
C(1′)	+0.007 (9)	B(9′)	−0.012 (12)
B(3′)	−0.015 (12)	Ni	−1.518 (3)
B(5′)	+0.003 (12)	Me(1′)	−0.386 (11)
B(8′)	+0.017 (12)		
β′ Plane: C(2′), B(6′), B(7′), B(10′), B(12′) $-0.1012X + 0.9871Y + 0.1239Z = +7.8311$			
C(2′)	+0.011 (12)	B(12′)	−0.041 (14)
B(6′)	+0.016 (13)	B(11′)	+0.936 (14)
B(7′)	−0.032 (13)	Me(2′)	+0.633 (12)
B(10′)	−0.036 (14)		
Dihedral angles: α/α′ = 14° 51′, α/β = 1° 24′, α′/β′ = 0° 00′			

[a] See footnote *a*, Table II. [b] Planes are defined as $c_1X + c_2Y + c_3Z = d$, where X, Y, Z are Cartesian coordinates which are related to the monoclinic cell coordinates (x, y, z) by the transformations: $X = xa + zc \cos\beta$, $Y = yb$, and $Z = zc \sin\beta$.

est being Ni–B(9′) = 2.107 ± 0.012 Å, and the longest being Ni–C(1′) = 2.163 ± 0.009 Å. Distances from the nickel to atoms of the α plane vary quite significantly: the nickel–carbon distances of 2.225 ± 0.009 Å and 2.195 ± 0.009 Å are significantly longer than the nickel–boron distances (2.092 ± 0.013 Å, 2.050 ± 0.013 Å, and 2.104 ± 0.013 Å). It appears, therefore, that the dihedral angle of 14° 51′ between α and α′ planes results primarily in asymmetric bonding of the nickel to the (3)-1,2-dimethyl-1,2-dicarbollide ligand. (Another measure of the tilting of the α plane relative to the α′ plane is the B(10)–Ni–B(11′) angle of 168.3 ± 0.3°.)

Average values for the various types of bond lengths and angles within the molecule are compiled in Table V(b) and Table VI, respectively. Root-mean-square deviations from the mean value have been calculated (see Table V(b), footnote *b*). Since the two ligands are nonidentical in position of coordination to the nickel ion, and in relative orientations within the molecule (*i.e.*, one ligand is symmetrically bonded while the other is not, *vide supra*), the large values of *some* overall rms deviations (*e.g.*, for nickel–boron bond lengths) probably reflect simply a chemical nonequivalence of averaged parameters.

The average B–B, B–C, and C–C distances of 1.742 ± 0.036 Å, 1.704 ± 0.030 Å, and 1.677 ± 0.057 Å, respectively, are in good agreement with values found in other icosahedral carborane derivatives, *i.e.*, in $(C_5H_5)Fe(B_9C_2H_{11})$,[17] $[(B_9C_2H_{11})Re(CO)_3^-]$,[18] $[Cu(B_9C_2H_{11})_2^{2-}]$,[19] $[Co(B_9C_2H_{11})_2^-]$,[20] $[Cu(B_9C_2H_{11})_2^-]$,[21] $[Co(B_9C_2H_8Br_3)^-]$,[22] $(B_9C_2H_{10})_2CoS_2CH$,[23] o-$B_{10}Br_2H_8C_2H_2$,[26] o-$B_{10}H_{10}(C_2H_2Br)_2$,[27] m-$B_{10}Br_2H_8C_2H_2$,[28] and o-$B_{10}Cl_8H_2C_2H_2$.[29] The average value for C–C bonds in the (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ icosahedra may be somewhat misleading since the C(1′)–C(2′) bond length of 1.717 ± 0.015 Å appears to be significantly longer than the more "normal" C(1)–C(2) distance of 1.636 ± 0.013 Å.

Within the triangular faces of the icosahedra, the 57 independent B–B–B bond angles have an average value of 60.0 ± 1.7°. The 16 C–B–B and 8 B–C–B angles average, respectively, 59.3 ± 1.4° and 61.5 ± 1.4°, while the 6 C–C–B and the 3 C–B–C angles are 60.4 ± 1.3° and 59.2 ± 2.1°. Angles of icosahedral faces involving the nickel atom are all lower, due to the greater Ni–B or Ni–C distance as compared with B–B, B–C, and C–C bond lengths. The C–Ni–C, C–Ni–B, B–Ni–B angles average 43.5 ± 0.4°, 47.5 ± 1.1°, and 50.0 ± 1.3°, respectively. This results in a corresponding increase in average Ni–C–C (68.3 ± 1.4°), Ni–C–B (63.7 ± 1.8°), Ni–B–C (68.9 ± 2.0°), and Ni–B–B (65.0 ± 1.2°) angles.

The average values of angles around the pentagonal rings are all consistent with those expected on the basis of distortions due to insertion of carbon atoms into the icosahedral framework, the protrusion of the nickel vertex, and the tilt of the $[(CH_3)_2B_9C_2H_9^{2-}]$ ligands relative to one another. As with angles around the triangular faces, they are in good agreement with the values reported for similar compounds.[17–18,20,22–23,26–29]

The CH_3–C–C angles are all within 5° of their average value of 117.2 ± 3.2°, while CH_3–C–B angles range from 113.3 ± 0.8° to 127.2 ± 0.8° and average 119.7 ± 4.7°. The CH_3–C–Ni angles are somewhat smaller,

Table VIII. Intermolecular Contacts (≤3.5Å) between (3,4′)-$[(CH_3)_2B_9C_2H_9]_2N^{IV}$ Molecules

Old atom	New atom	Transformation	Distance, Å
Me(1)	H(8)	$x + 1/2, -y + 1/2, z + 1/2$	3.46
Me(1)	H(5′)	$x + 1/2, -y + 1/2, z + 1/2$	3.40
Me(1)	H(12′)	$x + 1/2, -y + 1/2, z + 1/2$	3.50
Me(2)	H(4)	$x, y, z + 1$	3.17
Me(2)	H(9′)	$x + 1/2, -y + 1/2, z + 1/2$	3.39
Me(1′)	H(7)	$x + 1/2, -y + 1/2, z - 1/2$	3.34
Me(1′)	H(12)	$x + 1/2, -y + 1/2, z - 1/2$	3.26
Me(2′)	H(9)	$x + 1/2, -y + 1/2, z + 1/2$	3.28
Me(2′)	H(10)	$-x + 3/2, y + 1/2, -z + 1/2$	3.43
Me(2′)	H(11)	$-x + 3/2, y + 1/2, -z + 3/2$	3.22
B(11′)	H(10′)	$-x + 1, -y + 1, -z + 1$	3.34
H(4)	H(8′)	$x, y, z - 1$	3.21
H(5)	H(6′)	$-x + 3/2, y - 1/2, -z + 1/2$	2.99
H(5)	H(11′)	$-x + 3/2, y - 1/2, -z + 1/2$	3.08
H(6)	H(7′)	$-x + 3/2, y - 1/2, -z + 3/2$	3.24
H(6)	H(10′)	$x + 1/2, -y + 1/2, z + 1/2$	3.34
H(6)	H(11′)	$-x + 3/2, y - 1/2, -z + 3/2$	3.02
H(9)	H(11)	$x, y, z - 1$	3.39
H(10)	H(12)	$-x + 1, -y, -z + 1$	3.46
H(3′)	H(8)	$x + 1/2, -y + 1/2, z + 1/2$	2.89
H(3′)	H(9)	$x + 1/2, -y + 1/2, z + 1/2$	3.48
H(3′)	H(12)	$x + 1/2, -y + 1/2, z + 1/2$	3.18
H(5′)	H(8′)	$x, y, z - 1$	3.28
H(6′)	H(6)	$-x + 3/2, y + 1/2, -z + 1/2$	3.49
H(6′)	H(10)	$-x + 3/2, y + 1/2, -z + 1/2$	2.99
H(6′)	H(7′)	$x, y, z - 1$	3.36
H(7′)	H(10)	$-x + 3/2, y + 1/2, -z + 3/2$	3.27
H(7′)	H(12)	$x + 1/2, -y + 1/2, z + 1/2$	3.29
H(10′)	H(10′)	$-x + 1, -y + 1, -z + 1$	3.41
H(10′)	H(11′)	$-x + 1, -y + 1, -z + 1$	2.65
H(10′)	H(12′)	$-x + 1, -y + 1, -z + 1$	3.36

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averaging 115.8 ± 3.7°. There appear to be no significant distortions of the methyl groups from positions predicted from an idealized icosahedral geometry. Individual C–CH$_3$ bond lengths are: C(1)–CH$_3$(1) = 1.553 ± 0.014 Å, C(2)–CH$_3$(2) = 1.547 ± 0.014 Å, C(1′)–CH$_3$(1′) = 1.511 ± 0.014 Å, C(2′)–CH$_3$(2′) = 1.577 ± 0.017 Å. The average value of 1.547 ± 0.028 Å is not significantly different from the C(sp^3)–C(sp^3) distance of 1.5445 Å in diamond.[30]

Intermolecular Contacts

The packing of (3,4′)-[(CH$_3$)$_2$B$_9$C$_2$H$_9$]Ni^{IV} molecules within the unit cell is shown in Figure 2, which shows the view down *c*. Enantiomers are related to one another by an n-glide plane at *y* = 0.25, and by centers of symmetry at (0 or 0.5, 0 or 0.5, 0 or 0.5).

The individual molecules are separated by normal van der Waals distances. Quantitative data on intermolecular contacts are shown in Table VIII. Closest approaches (of each type) are methyl carbon···hydrogen = 3.17, boron···hydrogen = 3.34, and hydrogen···hydrogen = 2.65 Å. It should be emphasized, however, that hydrogen atoms of the methyl groups have not been included in these calculations.

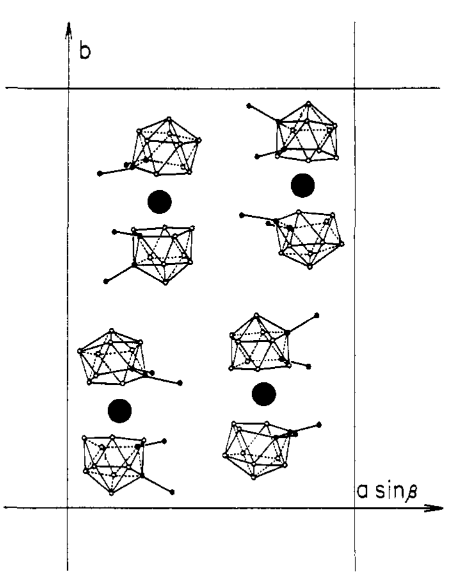

Figure 2. Packing of (3,4′)-[(CH$_3$)$_2$B$_9$C$_2$H$_9$]$_2$Ni^{IV} molecules in the unit cell, viewed down *c*.

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[30] "Interatomic Distances, Supplement," Special Publication No. 18, The Chemical Society, London, 1965, p S14s.

Crystal and Molecular Structure of Bis-(3)-1,7-dicarbollylnickelate(II) Dianion

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Abstract: The crystal and molecular structure of [CH$_3$N(C$_2$H$_4$)$_3$NCH$_3$][Ni(*neo*-C$_2$B$_9$H$_{11}$)$_2$] has been determined from a single-crystal X-ray diffraction study. The orthorhombic cell Fdd2 with a_0 = 16.95 (3), b_0 = 24.52 (7), and c_0 = 11.63 (4) Å contains only eight formula units (ρ = 1.30 g/cm^3); thus both the organic dication and carbametallic dianion are crystallographically required to possess twofold axes of symmetry. The structure was solved using 622 unique nonzero reflections collected by a film method, and refined by least-squares techniques to a final *R* factor of 10.5% based on *F*. While the carborane cages in the previously reported bis-(3)-1,2-dicarbollylnickelate(II) ion were grossly slipped with respect to one another to give an allyl-like structure, that distortion is nearly absent in the compound reported here. Although the (3)-1,7- and (3)-1,2-dicarbollide ions have the same symmetry, the atom charges in the former are believed to be more uniformly distributed. Thus, it appears that ligand asymmetry is a definite factor in the stereochemistry of the electron-rich metallobisdicarbollyls. A further feature of the structure is that the carborane cages are not related by a center of symmetry but, rather, have taken on an intermediate rotamer configuration. Although the N,N′-dimethyltriethylenediammonium ion possesses three different twofold axes of symmetry, none of them was found to lie along a crystallographic twofold axis. Thus, for no obvious reason, the organic dication is disordered.

A large number of transition metal derivatives of the (3)-1,2-dicarbollide ion have been synthesized and structurally characterized by single-crystal X-ray diffraction studies.[1] The stereochemistry of these compounds is of two distinct forms.

First, as exemplified by [π-C$_5$H$_5$]Fe[π(3)-1,2-C$_2$B$_9$H$_{11}$],[2] there are symmetrical π-sandwich structures which are extant when the metal in its "formal" valence possesses seven or fewer d electrons.

Second, for those compounds which formally contain d^8 or d^9 metal ions, a slipped π-sandwich or π-allyl stereochemistry is observed.[3]

A part of a continuing effort to learn more about the distortions in the electron-rich (d^7–d^9) series of compounds, the structure determination of the Ni^{2+} (d^8) complex of (3)-1,7-dicarbollide ion was undertaken.

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[3] R. M. Wing, *ibid.*, **90**, 4828 (1968).