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Crystal and Molecular Structure of the Asymmetric Metallocarborane Complex Tetraethylammonium (3,11′)-*commo*-[Undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborato][decahydro-9′-pyridyl-7′,8′-dicarba-11′-cobalta-*nido*-undecaborate], $[(C_2H_5)_4N^+][(B_9C_2H_{11})Co((B_8C_2H_{10})(C_5H_5N))^-]$

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The molecular structure of $[(C_2H_5)_4N^+][(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$ has been elucidated *via* a complete three-dimensional X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with $a = 16.903$ (15), $b = 10.771$ (10), $c = 15.990$ (14) Å, $\beta = 99.28$ (5)°, and $Z = 4$. Observed and calculated densities are 1.20 (2) and 1.205 g cm^{-3}, respectively. Diffraction data to $\sin\theta = 0.77$ (Cu Kα radiation) were collected with a Supper-Pace diffractometer and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. The final discrepancy index is $R_F = 6.7\%$ for the 2058 independent nonzero reflections. All atoms have been located except for one bridging hydrogen in the $B_8C_2H_{10}$ framework. The molecule consists of a cobalt(III) atom sandwiched between mutually staggered $(B_9C_2H_{11}^{\ 2-})$ and $(B_8C_2H_{10}py^{2-})$ ions. The B_8C_2 skeleton of the latter ion defines an icosahedron from which two adjacent apices have been removed; it is linked to the central cobalt(III) atom *via* an open four-atom (C–B–B–B) bonding face.

Introduction

Base degradation of the $[\{\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}_2(Co^{III})^-]$ anion with aqueous hydroxide ion (and in the presence of added Co^{2+} ion) has been shown to lead to the formation of such fused icosahedral species as $[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})^{2-}]$[1] and $[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_8C_2H_{10})Co(B_9C_2H_{11})^{3-}]$,[2] each of which has been shown crystallographically[3-5] to contain the π-bidentate $(B_8C_2H_{10}^{\ 4-})$ or "(3,6)-1,2-dicarbacanastide(4−)" ion. There is also evidence that higher congeners, containing additional $\{(B_8C_2H_{10})Co^-\}$ units, are formed in this reaction.[6]

More recently, Hawthorne and coworkers[7] have studied the base degradation and oxidation of $[\{\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}_2(Co^{III})^-]$ in detail and have found evidence for a π-monodentate $(B_8C_2H_{10}^{\ 2-})$ ion and derivatives thereof. We have undertaken a single-crystal X-ray structural analysis of $[(C_2H_5)_4N^+][(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$, the anion of which is derived *via* the route[7]

$$[(B_9C_2H_{11})_2Co^-] \xrightarrow[2.\ H_2O_2]{1.\ OH^-} [(B_9C_2H_{11})Co(B_8C_2H_{10})^-] \xrightarrow{C_5H_5N} [(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$$

The dramatic color change (bright blue → bright red)[6] in going from $[(B_9C_2H_{11})Co(B_8C_2H_{10})^-]$ to $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$, coupled with the observation that the reaction is not "instantaneous" ($t_{1/2} \approx 15$ min), in contrast to most simple addition reactions, suggests that the addition of pyridine leads to some significant change in the bonding of the B_8C_2 ligand to the central cobalt atom. Hawthorne, *et al.*,[7] have suggested a closo geometry for the $\{(B_8C_2H_{10})Co\}$ moiety in the $[(B_9C_2H_{11})Co(B_8C_2H_{10})^-]$ anion. Our structural results on the pyridine adduct are reported below. A preliminary communication of this work has appeared previously.[8]

Unit Cell and Space Group

A sample of the complex was supplied by Professor M. F. Hawthorne and Dr. J. N. Francis. The complex is air stable and does not decompose upon exposure to X-rays.

Optical examination and preliminary X-ray diffraction photographs of the red crystalline parallelepipeds indicated that they belong to the monoclinic system. A subsequent survey of $(0\text{-}2)kl$, $h0l$ Weissenberg photographs and $h(0\text{-}2)l$, $hk(0\text{-}2)$ precession photographs (all taken with Cu Kα radiation) revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent with the centrosymmetric space group $P2_1/c$ (C_{2h}^5; No. 14).

Unit cell parameters (from calibrated zero-level precession photographs) are $a = 16.903$ (15) Å, $b = 10.771$ (10) Å, $c = 15.990$ (14) Å, and $\beta = 99.28$ (5)°. The unit cell volume is 2873 Å^3. The observed density ($\rho_{obsd} = 1.20 \pm 0.02$ g cm^{-3}) is in excellent agreement with the value calculated for $M = 521.47$ and $Z = 4$ ($\rho_{calcd} = 1.205$ g cm^{-3}).

No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Diffraction Data

Intensity data were collected with a scintillation counter used in conjunction with a Supper-Pace "Buerger automated diffractometer" using a "stationary-background, ω-scan, stationary-background" counting sequence and equiinclination Weissenberg geometry. The experimental procedure has been described previously.[9] Details specific to the present analysis include the following: (i) Cu Kα radiation ($\bar{\lambda}$ 1.5418 Å) was used; (ii) the angle scanned was chosen as $w(hkl) = [1.50 + 1.00L(hkl)]°$, where $(1/L(hkl))$ is the multiplicative Lorentz factor for the reflection hkl.

Two crystals were used during analysis. Crystal I (0.12 × 0.30 × 0.42 mm) was aligned along the b axis, and crystal II (0.11 × 0.38 × 0.52 mm) was aligned along the a axis. (Dimensions refer sequentially to a, b, c.) A total of 2992 reflections in quadrants hkl and $\bar{h}kl$ of levels $h(0\text{-}11)l$ was collected from crystal I; 2563 reflections in quadrants hkl and $hk\bar{l}$ of levels $(0\text{-}9)kl$ were collected from crystal II. [This represents data complete to $\sin\theta = 0.77$ and includes all data visible on long-exposure Weissenberg photographs.] $I(hkl)$, the intensity of the reflection hkl, and $\sigma\{I(hkl)\}$, its estimated standard deviation, were calculated in the normal fashion.[10]

All data were adjusted for Lorentz and polarization effects and

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Table II. Final Atomic Positions[a]

Atom	x	y	z	Atom	x	y	z
(A) Atoms in Metallocarborane Anion							
Co	0.23747 (7)	0.23503 (9)	0.19116 (8)	B(1′)	0.0952 (7)	0.0339 (8)	0.2159 (7)
C(1)	0.3350 (5)	0.1946 (7)	0.1337 (6)	B(2′)	0.1784 (6)	0.1173 (8)	0.2639 (6)
C(2)	0.3485 (5)	0.1587 (7)	0.2320 (5)	B(3′)	0.0829 (7)	0.1596 (10)	0.2822 (7)
C(7′)	0.1500 (5)	0.2648 (7)	0.2606 (5)	B(4′)	0.0170 (6)	0.1414 (9)	0.1863 (7)
C(8′)	0.0668 (5)	0.2837 (7)	0.2124 (5)	B(5′)	0.0709 (6)	0.0858 (8)	0.1099 (7)
B(4)	0.3035 (6)	0.3476 (8)	0.1208 (6)	B(6′)	0.1731 (6)	0.0687 (8)	0.1553 (7)
B(5)	0.4035 (6)	0.3033 (9)	0.1168 (7)	B(9′)	0.0529 (5)	0.2450 (8)	0.1146 (6)
B(6)	0.4325 (6)	0.1824 (9)	0.1880 (8)	B(10′)	0.1413 (6)	0.1927 (8)	0.0859 (6)
B(7)	0.3266 (6)	0.2759 (9)	0.2907 (6)	py(N)	−0.0159 (4)	0.3085 (6)	0.0486 (5)
B(8)	0.2990 (6)	0.4032 (8)	0.2237 (7)	py(1)	−0.0524 (5)	0.4119 (7)	0.0680 (6)
B(9)	0.3854 (6)	0.4361 (8)	0.1758 (7)	py(2)	−0.1091 (5)	0.4691 (7)	0.0095 (6)
B(10)	0.4624 (6)	0.3332 (10)	0.2181 (8)	py(3)	−0.1285 (6)	0.4201 (9)	−0.0714 (6)
B(11)	0.4258 (6)	0.2340 (9)	0.2891 (7)	py(4)	−0.0908 (6)	0.3117 (8)	−0.0906 (6)
B(12)	0.3972 (6)	0.3895 (9)	0.2829 (7)	py(5)	−0.0340 (5)	0.2616 (7)	−0.0301 (6)
(B) Atoms in NEt_4^+ Cation							
N	0.6862 (4)	0.2297 (5)	0.0644 (4)	Et(3a)	0.6841 (6)	0.3669 (8)	0.0419 (6)
Et(1a)	0.6187 (6)	0.1614 (8)	0.0106 (7)	Et(3b)	0.6113 (6)	0.4353 (8)	0.0515 (7)
Et(1b)	0.6189 (7)	0.1637 (9)	−0.0842 (7)	Et(4a)	0.6746 (6)	0.2112 (8)	0.1554 (6)
Et(2a)	0.7661 (6)	0.1790 (8)	0.0482 (6)	Et(4b)	0.7384 (8)	0.2694 (9)	0.2195 (7)
Et(2b)	0.7836 (6)	0.0452 (8)	0.0676 (6)				
(C) Calculated Positions for Hydrogen Atoms[b]							
H(1)	0.3156	0.1337	0.0871	H1a(1)	0.5668	0.1994	0.0213
H(2)	0.3369	0.2159	0.2496	H1a(2)	0.6212	0.0720	0.0294
H(4)	0.2669	0.3815	0.0706	H1b(1)	0.5714	0.1155	−0.1139
H(5)	0.4270	0.3117	0.0635	H1b(2)	0.6700	0.1248	−0.0968
H(6)	0.4719	0.1173	0.1774	H1b(3)	0.6155	0.2522	−0.1049
H(7)	0.3031	0.2675	0.3440	H2a(1)	0.8095	0.2291	0.0836
H(8)	0.2596	0.4683	0.2342	H2a(2)	0.7687	0.1919	−0.0137
H(9)	0.3969	0.5225	0.1583	H2b(1)	0.8382	0.0238	0.0541
H(10)	0.5200	0.3584	0.2250	H2b(2)	0.7419	−0.0079	0.0323
H(11)	0.4624	0.2001	0.3393	H2b(3)	0.7826	0.0293	0.1295
H(12)	0.4164	0.4500	0.3292	H3a(1)	0.6916	0.3740	−0.0193
H(1′)	0.0836	−0.0522	0.2341	H3a(2)	0.7304	0.4081	0.0792
H(2′)	0.2171	0.0778	0.3101	H3b(1)	0.6171	0.5246	0.0347
H(3′)	0.0660	0.1500	0.3389	H3b(2)	0.6027	0.4312	0.1123
H(4′)	−0.0403	0.1171	0.1851	H3b(3)	0.5639	0.3971	0.0140
H(5′)	0.0463	0.0300	0.0628	H4a(1)	0.6740	0.1193	0.1670
H(6′)	0.2068	0.0006	0.1372	H4a(2)	0.6214	0.2485	0.1626
H(7′)	0.1748	0.3210	0.3080	H4b(1)	0.7265	0.2530	0.2783
H(8′)	0.0328	0.3524	0.2307	H4b(2)	0.7396	0.3617	0.2095
H(10′)	0.1582	0.2022	0.0291	H4b(3)	0.7921	0.2325	0.2139
H(py1)	−0.0355	0.4504	0.1282				
H(py2)	−0.1374	0.5474	0.0256				
H(py3)	−0.1695	0.4670	−0.1154				
H(py4)	−0.1052	0.2710	−0.1494				
H(py5)	−0.0045	0.1816	−0.0433				

[a] Estimated standard deviations, shown in parentheses, are right adjusted to the least significant digit of the preceding number. [b] Distances of B–H = 1.00 Å and C–H = 1.08 Å were used in calculating the positions of hydrogen atoms. (See also text and ref 15 and 17.) In retrospect, a C–H distance of ~0.95 Å would more accurately have described the position of the *electron density* maxima for the C-bonded hydrogen atoms: M. R. Churchill, submitted for publication in *Inorg. Chem.*

absorption corrections were applied[11] ($\mu = 46.00$ cm^{-1} for Cu Kα radiation). The transmission coefficients ranged from 0.352 to 0.593 for data from crystal I (volume 7.4×10^{-6} cm^3) and from 0.238 to 0.489 for data from crystal II (volume 10.8×10^{-6} cm^3). The 22 levels of data were merged to a common scale by a least-squares procedure which minimized a sum of residuals linear in the logarithms of the individual scale factors.[12] (The overall R factor for scaling was 5.7% based on F^2.) The resulting 2058 independent nonzero reflections were used in calculating a Wilson plot,[13] from which were obtained an approximate absolute scale factor and the overall isotropic thermal parameter ($\bar{B} = 2.15$ Å^2).

Solution and Refinement of the Structure

The coordinates of the cobalt atom were obtained from a three-dimensional Patterson synthesis which had been sharpened such that the average intensity was independent of sin θ and which had the origin peak removed. The proximity of the cobalt y coordinate to $^1/_4$, however, resulted in an ambiguity in the z coordinate of this atom. The source of this confusion is revealed by inspection of the Patterson vectors for space group $P2_1/c$: A, $\pm[0, {}^1/_2 + 2y, {}^1/_2]$ (multiplicity 2); B, $\pm[2x, 2y, 2z]$ (multiplicity 1); C, $\pm[2x, -2y, 2z]$ (multiplicity 1); D, $\pm[2x, {}^1/_2, {}^1/_2 + 2z]$ (multiplicity 2).

For $y \approx {}^1/_4$, near-overlap of vectors B and C gives rise to peaks approximating multiplicity 2 and falling on the Harker section defined by vector D. In theory, deviation of the Patterson peaks resulting from coincidence of vectors B and C, from spherical symmetry along y, should distinguish them from vector D, and unique assignment of B, C, and D can be made on this basis. In the case under investigation, this "elongation" of overlapped peaks was not completely obvious and correct assignment was made by trial and error. [It is of interest to note that the incorrect assignment, *i.e.*, $x_{Co} = 0.238$, $y_{Co} = 0.240$, $z_{Co} = 0.058$, resulted in an initial Fourier synthesis (R_F = 49.2%)[14] which yielded a rather poorly defined, false, but chemically sensible solution.]

A three-dimensional Fourier synthesis, phased by the cobalt atom in its correct position, *i.e.*, $x_{Co} = 0.238$, $y_{Co} = 0.240$, $z_{Co} = 0.193$ (R_F = 48.7%) yielded the positions of all other nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters for all 37 nonhydrogen atoms (assuming

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(14) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4$.

Table IIIa. Anisotropic Thermal Parameters[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	12.5 (0.5)	34.2 (1.0)	17.9 (0.6)	1.6 (1.4)	1.3 (0.8)	−2.4 (1.5)
C(1)	27 (5)	55 (8)	46 (6)	18 (9)	19 (8)	−7 (11)
C(2)	20 (4)	60 (8)	31 (5)	24 (9)	−7 (7)	13 (10)
C(7′)	15 (4)	66 (8)	26 (4)	9 (9)	8 (6)	−6 (10)
C(8′)	28 (4)	56 (7)	30 (4)	19 (10)	5 (7)	5 (10)
B(4)	26 (5)	69 (9)	11 (5)	16 (11)	−5 (8)	18 (10)
B(5)	24 (5)	76 (10)	33 (6)	−27 (12)	18 (9)	24 (12)
B(6)	19 (5)	55 (9)	54 (7)	26 (11)	1 (10)	25 (13)
B(7)	17 (4)	75 (9)	22 (5)	−2 (11)	−18 (7)	15 (12)
B(8)	25 (5)	37 (8)	35 (6)	6 (10)	9 (8)	−5 (11)
B(9)	19 (5)	52 (9)	47 (6)	−9 (11)	6 (9)	10 (13)
B(10)	17 (5)	79 (10)	55 (7)	−7 (12)	9 (10)	25 (14)
B(11)	20 (4)	92 (11)	29 (5)	−21 (13)	−10 (8)	20 (14)
B(12)	24 (5)	76 (10)	32 (6)	−7 (12)	−9 (9)	−4 (13)
B(1′)	33 (5)	49 (8)	40 (6)	−12 (12)	16 (9)	23 (12)
B(2′)	23 (5)	49 (8)	28 (5)	7 (11)	7 (8)	22 (11)
B(3′)	32 (6)	82 (10)	30 (6)	−8 (13)	26 (9)	47 (13)
B(4′)	24 (5)	63 (9)	38 (6)	−27 (12)	15 (9)	−1 (12)
B(5′)	28 (5)	51 (9)	27 (5)	5 (11)	−1 (8)	6 (11)
B(6′)	20 (5)	34 (8)	36 (5)	8 (10)	4 (8)	−11 (11)
B(9′)	16 (4)	75 (10)	17 (4)	19 (12)	−5 (7)	18 (11)
B(10′)	29 (5)	65 (9)	22 (5)	73 (11)	15 (8)	−1 (11)
py(N)	17 (3)	68 (7)	35 (4)	−5 (8)	1 (6)	8 (9)
py(1)	26 (4)	50 (8)	38 (5)	14 (10)	8 (8)	−9 (11)
py(2)	27 (4)	59 (8)	37 (5)	31 (10)	7 (8)	17 (11)
py(3)	28 (5)	103 (10)	39 (6)	21 (12)	5 (8)	25 (13)
py(4)	26 (4)	93 (10)	24 (5)	17 (11)	−14 (7)	−2 (11)
py(5)	31 (4)	64 (8)	27 (5)	−4 (11)	11 (7)	−27 (12)
N	26 (3)	50 (6)	26 (3)	2 (8)	10 (5)	8 (8)
Et(1a)	28 (5)	90 (9)	56 (7)	−15 (12)	−13 (9)	10 (13)
Et(1b)	74 (7)	106 (11)	39 (6)	38 (15)	−52 (10)	−24 (14)
Et(2a)	28 (5)	95 (10)	36 (5)	1 (11)	9 (8)	3 (11)
Et(2b)	44 (5)	91 (10)	48 (6)	50 (12)	3 (9)	−24 (12)
Et(3a)	43 (5)	79 (9)	28 (5)	−4 (12)	18 (8)	20 (11)
Et(3b)	54 (6)	79 (9)	53 (6)	34 (12)	56 (10)	39 (12)
Et(4a)	45 (5)	85 (9)	36 (5)	25 (11)	44 (9)	26 (12)
Et(4b)	92 (8)	108 (11)	39 (6)	−31 (17)	15 (11)	−15 (14)

[a] See footnote *a* of Table II. The anisotropic thermal parameter, T, is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The atom vibration ellipsoids are illustrated in the figures.

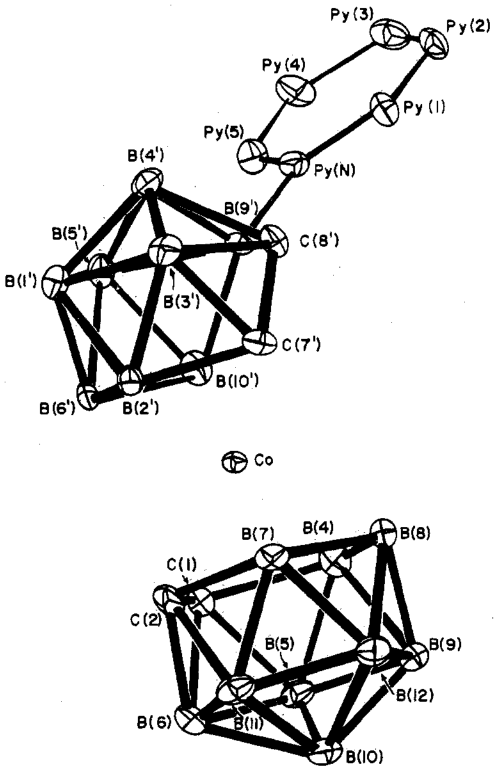

Figure 1. The $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$ ion, projected on (001).

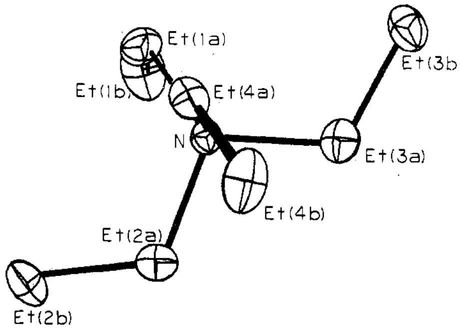

Figure 2. The $[(C_2H_5)_4N^+]$ ion, projected on (001).

all cage atoms to be boron) led to convergence at $R_F = 11.4\%$, $R_{wF^2} = 7.7\%$.[14] Examination of isotropic thermal parameters of the cage atoms showed four to be significantly smaller than the others, *i.e.*, *ca.* 0.9 Å^2 compared to *ca.* 2.4 Å^2. A Fourier synthesis also showed these same four atoms to have higher electron densities than other cage atoms. These atoms were therefore redefined as carbon atoms for subsequent crystallographic processes. A further two cycles of refinement of positional and isotropic thermal parameters converged to $R_F = 9.3\%$ and $R_{wF^2} = 5.2\%$. A difference-Fourier synthesis at this stage revealed evidence of anisotropic thermal motion for most atoms and also indicated the positions of 20 of the 21 cage hydrogens, plus all of those on the pyridine ring. [Peak heights, in e Å^{-3} × 100 were as follows: H(1), 47; H(2), 43; H(4), 58; H(5), 41; H(6), 42; H(7), 42; H(8), 61; H(9), 52; H(10), 46; H(11), 54; H(12), 71; H(1′), 48; H(2′), 70; H(3′), 60; H(4′), 36; H(5′), 61; H(6′), 52; H(7′), 39; H(8′), 38; H(10′), 55; H(py1), 60; H(py2), 54; H(py3), 70; H(py4), 47; H(py5), 63. These may be compared with carbon peak heights of *ca.* 5.0 e Å^{-3} on an "observed" Fourier synthesis at this stage.] A subsequent structure factor calculation, including all hydrogens listed above, yielded reduced discrepancy indices of $R_F = 8.9\%$ and $R_{wF^2} = 5.0\%$. Refinement was continued using anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms (as listed

Table IIIb. Direction Cosines for Atomic Vibration Ellipsoids[a]

Atom	$(\overline{U^2})_{max}$ (dc's, major axis)	$(\overline{U^2})_{med}$ (dc's, median axis)	$(\overline{U^2})_{min}$ (dc's, minor axis)
Co	2.45 (442, 300, −906)	1.97 (26, −946, −323)	1.70 (−897, 121, −275)
C(1)	5.91 (117, −74, 959)	4.34 (768, 639, −167)	2.47 (−630, 766, 231)
C(2)	4.70 (−645, −197, 833)	4.18 (295, 828, 424)	1.66 (−705, 525, −356)
C(7′)	4.07 (212, 923, −353)	3.20 (123, 303, 913)	1.94 (970, −240, −205)
C(8′)	4.60 (842, 506, −322)	3.86 (1, 348, 925)	2.66 (540, −789, 202)
B(4)	4.65 (634, 771, −35)	3.76 (−734, 572, 481)	0.97 (244, −283, 876)
B(5)	5.65 (371, −820, −491)	4.35 (−566, 173, −705)	1.80 (−736, −546, 513)
B(6)	7.28 (186, −210, 977)	4.12 (−662, −749, 142)	1.58 (726, −629, 158)
B(7)	5.06 (−500, 669, 623)	3.90 (546, 736, −483)	1.17 (673, −100, 615)
B(8)	4.50 (−152, −116, 993)	3.56 (964, 202, 15)	2.07 (−218, 973, 115)
B(9)	6.13 (191, −166, −986)	3.25 (543, −803, 154)	2.39 (−818, −572, 70)
B(10)	7.49 (−132, 375, 927)	4.25 (144, −909, 364)	2.29 (−981, −184, 93)
B(11)	6.48 (435, −791, −495)	3.62 (−408, −599, 746)	2.10 (−803, −124, −446)
B(12)	5.20 (664, −83, −840)	4.53 (79, −981, 165)	2.53 (−743, −178, −517)
B(1′)	5.43 (21, 350, 921)	4.82 (−950, 300, 64)	2.25 (−312, −888, 384)
B(2′)	4.16 (58, 592, 784)	3.30 (984, 105, −304)	2.14 (−171, 799, −541)
B(3′)	6.41 (−75, −773, −610)	4.85 (−894, 332, −154)	1.56 (−443, −540, 778)
B(4′)	4.97 (−474, 493, −644)	4.57 (432, −591, −742)	2.23 (−767, −638, 190)
B(5′)	4.53 (870, 17, −627)	3.36 (361, 659, 593)	2.69 (−336, 752, −506)
B(6′)	4.75 (−292, −200, 970)	2.86 (905, 259, 187)	1.78 (−310, 945, 154)
B(9′)	4.74 (249, 947, 159)	2.99 (−761, 63, 760)	1.19 (599, −315, 630)
B(10′)	4.39 (833, 474, 148)	3.67 (−396, 871, −222)	2.53 (−387, 128, 964)
py(N)	4.83 (−303, 430, 888)	3.82 (35, 897, −441)	2.36 (953, 103, 129)
py(1)	5.02 (306, 285, −946)	3.92 (−804, −434, −272)	2.49 (510, −855, −177)
py(2)	5.18 (−500, −635, −501)	4.71 (615, 220, −847)	2.10 (610, −741, 178)
py(3)	6.75 (−175, −875, −417)	4.87 (633, 251, −825)	3.32 (−754, 413, −382)
py(4)	6.05 (−547, −792, 356)	4.58 (611, −599, −609)	1.98 (−572, 117, −709)
py(5)	4.83 (281, −712, 589)	4.37 (−956, −268, 274)	2.43 (86, −649, −260)
N	3.68 (858, 260, 299)	3.41 (−514, 477, 787)	2.69 (26, 840, −540)
Et(1a)	8.33 (491, −235, −907)	5.20 (90, −944, 299)	3.23 (−866, −232, −297)
Et(1b)	14.59 (874, 249, −552)	5.65 (−241, 968, 111)	2.89 (421, 37, 826)
Et(2a)	5.59 (−6, −993, −116)	4.60 (206, 115, −992)	4.00 (−979, 30, −44)
Et(2b)	8.95 (−696, −595, 509)	5.57 (−397, −149, −830)	3.30 (599, −790, −228)
Et(3a)	6.07 (−971, 92, −62)	5.10 (21, −887, −458)	2.86 (239, 452, −887)
Et(3b)	10.20 (−650, −356, −558)	4.26 (739, −499, −566)	3.68 (−175, −791, 607)
Et(4a)	8.07 (−706, −422, −448)	4.35 (437, −892, 47)	2.73 (558, 164, −893)
Et(4b)	13.38 (−981, 189, 117)	6.34 (190, 901, −415)	4.64 (36, 390, 902)

[a] The values of $(\overline{U^2})$, *i.e.*, the mean-square displacements (Å^2) along the principal axes of the atomic vibration ellipsoids, have been multiplied by 100. Direction cosines (dc's) are referred to the monoclinic axes and have been multiplied by 1000. The orientations of the atomic vibration ellipsoids are illustrated in Figures 1 and 2.

above) were included in calculated positions[15] with an isotropic thermal parameter of 2.3 Å^2. Neither the positions nor the thermal parameters of the hydrogens were allowed to refine. Hydrogen positions were, however, redefined with respect to new carbon and boron positions after each cycle of refinement. Three cycles of "three-matrix"[16] least-squares refinement of positional and anisotropic thermal parameters resulted in discrepancy indices of R_F = 7.6% and R_{wF^2} = 3.5%. A three-dimensional difference Fourier synthesis now revealed positions of all hydrogens in the tetraethylammonium cation. [Peak heights, in e Å^{-3} × 100, were as follows: H1a(1), 54; H1a(2), 39; H1b(1), 70; H1b(2), 43; H1b(3), 40; H2a(1), 58; H2a(2), 62; H2b(1), 37; H2b(2), 41; H2b(3), 43; H3a(1), 46; H3a(2), 54; H3b(1), 61; H3b(2), 37; H3b(3), 40; H4a(1), 36; H4a(2), 39; H4b(1), 51; H4b(2), 47; H4b(3), 41.] There was no evidence of the final B_8C_2 cage hydrogen on this Fourier synthesis. A subsequent structure factor calculation resulted in reduced discrepancy indices of R_F = 7.1% and R_{wF^2} = 3.2%. A further three cycles of "three-matrix" least-squares refinement of positional and anisotropic thermal parameters for nonhydrogen atoms led to final convergence $[(\Delta/\sigma)_{max} < 0.1]$ at R_F = 6.7% and R_{wF^2} = 2.7%. [Cage and pyridine hydrogen atoms were treated as described above. Positions of ethyl hydrogens were very close to those calculated[17] and were therefore included in these positions with d(C–H) = 1.08 Å and isotropic thermal parameters of 3.0 Å^2. Positions were updated after each cycle of refinement.]

A final difference Fourier synthesis showed no peaks greater than 0.4 e Å^{-3} (*nor the position of the final B_8C_2 cage hydrogen*), 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 1.46.

Scattering factors for neutral nitrogen, carbon, boron, and hydrogen were taken from the compilation of Ibers;[18a] the Thomas–Fermi–Dirac values for neutral cobalt[18b] were corrected for the real and imaginary components of dispersion ($\Delta f'$(Co) = −2.2 e, $\Delta f''$(Co) = +3.9 e).[18c] The function $w(|F_o|^2 - |F_c|^2)^2$ was minimized during least-squares refinement processes; here, $w(hkl) = [\sigma\{F^2(hkl)\}]^{-2}$. All calculations were performed on the Harvard University IBM 360/65 computer using Marsh's CRYM system of crystallographic subroutines.

The final observed and calculated structure factors are listed in Table I.[19] Atomic fractional coordinates are collected in Table II. Anisotropic thermal parameters are listed in Table IIIa; atomic vibration ellipsoids are defined in Table IIIb.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are listed in Table IVa. Average bond distances, with their root-mean-square deviations, are collected in Table

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(15) The calculated positions, assuming idealized icosahedral geometry, are all close to the center of the hydrogen peaks observed on the 9.3% difference Fourier.

(16) Matrix 1 included the scale factor and positional and thermal parameters for Co and all nonhydrogen Et_4N^+ atoms; matrix 2 included positional and thermal parameters for C(1), C(2), B(4)–B(12); positional and thermal parameters for C(7′), C(8′), B(1′)–B(6′), B(9′), B(10′), py(N), and py(1)–py(5) were contained in matrix 3.

(17) Positions of hydrogens on terminal, C(b), carbons of ethyl groups in Et_4N^+ were calculated such that the terminal CH_3 group and its adjacent CH_2 group were in a staggered conformation.

(18) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962: (a) pp 202-203; (b) p 210; (c) p 214.

(19) Table I, a listing of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1157.

Table IVa. Interatomic Distances[a]

Atoms	Distance, Å	Atoms	Distance, Å
(I) Distances within the $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10}py)^-]$ Ion			
(A) Distances from Cobalt Atom			
Co-C(1)	2.059 (9)	Co-B(8)	2.111 (9)
Co-C(2)	2.057 (8)	Co-B(2′)	2.082 (10)
Co-C(7′)	2.014 (8)	Co-B(10′)	2.191 (10)
Co-B(4)	2.094 (10)	Co-B(6′)	2.126 (9)
Co-B(7)	2.056 (10)		
(B) Carbon-Carbon Distances			
C(1)-C(2)	1.598 (13)	C(7′)-C(8′)	1.504 (12)
(C) Carbon-Boron Distances			
C(1)-B(4)	1.734 (12)	C(7′)-B(2′)	1.658 (12)
C(1)-B(5)	1.699 (13)	C(7′)-B(3′)	1.677 (13)
C(1)-B(6)	1.739 (14)	C(8′)-B(3′)	1.734 (13)
C(2)-B(6)	1.702 (14)	C(8′)-B(9′)	1.600 (12)
C(2)-B(7)	1.651 (12)	C(8′)-B(4′)	1.765 (13)
C(2)-B(11)	1.677 (13)		
(D) Boron-Boron Bond Lengths			
B(4)-B(5)	1.768 (15)	B(2′)-B(3′)	1.745 (15)
B(4)-B(8)	1.763 (14)	B(2′)-B(6′)	1.802 (14)
B(4)-B(9)	1.791 (14)	B(2′)-B(1′)	1.740 (14)
B(5)-B(6)	1.747 (14)	B(3′)-B(1′)	1.753 (15)
B(5)-B(9)	1.768 (14)	B(3′)-B(4′)	1.754 (15)
B(5)-B(10)	1.789 (16)	B(9′)-B(10′)	1.727 (14)
B(6)-B(10)	1.746 (14)	B(9′)-B(4′)	1.776 (14)
B(6)-B(11)	1.730 (16)	B(9′)-B(5′)	1.745 (13)
B(7)-B(8)	1.757 (13)	B(10′)-B(6′)	1.763 (13)
B(7)-B(11)	1.741 (14)	B(10′)-B(5′)	1.742 (14)
B(7)-B(12)	1.727 (14)	B(6′)-B(1′)	1.795 (15)
B(8)-B(9)	1.790 (15)	B(6′)-B(5′)	1.772 (15)
B(8)-B(12)	1.779 (15)	B(1′)-B(4′)	1.764 (15)
B(9)-B(10)	1.759 (15)	B(1′)-B(5′)	1.769 (15)
B(9)-B(12)	1.765 (15)	B(4′)-B(5′)	1.744 (15)
B(10)-B(11)	1.743 (15)		
B(10)-B(12)	1.739 (15)		
B(11)-B(12)	1.743 (14)		
(E) Interannular Contacts			
C(1)···B(10′)	3.240 (14)	B(7)···C(7′)	2.949 (12)
C(1)···B(6′)	3.123 (13)	B(7)···B(2′)	3.006 (14)
C(2)···B(2′)	3.034 (13)	B(8)···C(7′)	3.066 (13)
C(2)···B(6′)	3.172 (13)	B(4)···B(10′)	3.180 (14)
		C(7′)···B(10′)	2.880 (13)
(F) Distances involving C_5H_5N Substituent			
py(N)-B(9′)	1.592 (11)	py(2)-py(3)	1.387 (14)
py(N)-py(1)	1.335 (10)	py(3)-py(4)	1.388 (13)
py(N)-py(5)	1.345 (11)	py(4)-py(5)	1.360 (13)
py(1)-py(2)	1.372 (13)		
(II) Distances within $(C_2H_5)_4N^+$ Ion			
(A) Nitrogen-Carbon Distances			
N-Et(1a)	1.505 (12)	N-Et(3a)	1.520 (10)
N-Et(2a)	1.518 (12)	N-Et(4a)	1.512 (12)
(B) Carbon-Carbon Distances			
Et(1a)-Et(1b)	1.516 (16)	Et(3a)-Et(3b)	1.464 (14)
Et(2a)-Et(2b)	1.493 (13)	Et(4a)-Et(4b)	1.500 (15)

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

Table IVb. Average Bond Lengths

Atoms	No.	Range,[a] Å	Av,[b] Å
(A) Bonds within the Anion			
Co-C	3	2.014 (8)-2.059 (9)	2.043 (25)
Co-B	6	2.056 (10)-2.191 (10)	2.110 (46)
C(cage)-C(cage)	2	1.504 (12)-1.598 (13)	1.551 (65)
C-B	11	1.600 (12)-1.765 (13)	1.694 (48)
B-B	33	1.727 (14)-1.802 (14)	1.759 (20)
B-N(py)	1	1.592 (11)	1.592
C(py)-C(py)	4	1.360 (13)-1.388 (13)	1.377 (13)
C(py)-N(py)	2	1.335 (10)-1.345 (11)	1.340 (7)
(B) Bonds within the Cation			
N-C	4	1.505 (12)-1.520 (10)	1.514 (7)
C-C	4	1.464 (14)-1.516 (16)	1.493 (22)

[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 $\sigma^2 = [\Sigma_{i=1}{}^{i=N}(\chi_i - \bar{\chi})^2]/(N-1)$ where χ_i is the *i*th bond length and $\bar{\chi}$ is the mean of the *N* equivalent bond lengths.

IVb. Individual bond angles (with esd's) are given in Table Va; Table Vb contains average bond angles. Figures 1 and 2 show the $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$ and $(C_2H_5)_4N^+$ ions, respectively, projected on (001) and illustrate the labeling of all nonhydrogen atoms. Hydrogen atoms have been omitted from these diagrams for the sake of clarity and are numbered similarly to the boron and carbon atoms to which they are attached.

The $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$ ion consists of a d^6 Co(III) ion "sandwiched" between two mutually staggered carborane ligands. Bonding between the $[(3)\text{-}1,2\text{-}B_9C_2H_{11}{}^{2-}]$ ligand and the metal atom is identical with that observed in other symmetrical 1,2-dicarbollide complexes (*cf.* ref 20-26). The B_8C_2 skeleton of the $[B_8C_2H_{10}py^{2-}]$ ligand defines an icosahedron from which two adjacent apices have been removed. The skeleton has an open six-atom V-shaped face defined by C(7′), B(2′), B(6′), B(10′), B(9′), and C(8′) (see Figure 1). Coordination of the $[B_8C_2H_{10}py^{2-}]$ ligand to the central cobalt(III) atom occurs *via* the four-atom plane (α′—see Table VI) defined by C(7′)-B(2′)-B(6′)-B(10′). This four-atom system is planar (root-mean-square deviation of the constituent atoms is only 0.003 Å), but individual cobalt-(ligand atom) distances vary appreciably, with Co-C(7′) = 2.014 (8), Co-B(2′) = 2.082 (10), Co-B(6′) = 2.126 (9), Co-B(10′) = 2.191 (10) Å. The pyridine substituent is N bonded to B(9′), with py(N)-B(9′) = 1.592 (11) Å.

It should be noted that electronic considerations lead to the prediction that a more stable complex would be formed were the cobalt(III) atom to be bonded to the four-atom plane containing *both* carbon atoms (*i.e.*, C(7′)-C(8′)-B(9′)-B(10′); this possibility would, however, result in substantial repulsive interactions between the pyridine substituent on B(9′) and neighboring hydrogen atoms on the pentagonal bonding face of the (3)-1,2-dicarbollide ion.

The orientation of the B_8C_2 skeleton is similar to that of the (4)-1,2-dimethyl-1,2-dicarbollide dianion in (3,4′)-$[(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ [27] save that a boron atom ["B(12′)," using the numbering of Figure 1] is missing from the present $\{B_8C_2Co\}$ icosahedral fragment.

The anion in the present molecule may be named systematically as (3,11′)-*commo*-[undecahydro-1,2-dicarba-3-cobalta-*closo*-dodecaborato][decahydro-9′-pyridyl-7′,8′-dicarba-11′-cobalta-*nido*-undecaborate](1−).

The observed diamagnetism of the complex suggests that the d^6 Co(III) ion receives six electrons from the four-atom bonding face of the B_8C_2 ligand, as well as from the pentag-

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Table Va. Interatomic Angles[a]

Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg
(I) Angles within the Metallocarborane Anion							
(A) Angles between Cobalt and Atoms in the α, α′ Planes							
C(1)–Co–C(7′)	172.8 (3)	B(8)–Co–B(6′)	178.2 (4)	B(7)–Co–B(6′)	132.0 (4)	B(4)–Co–B(6′)	129.6 (4)
B(7)–Co–B(10′)	179.2 (4)	B(4)–Co–B(2′)	176.5 (4)	C(1)–Co–B(10′)	99.3 (4)	B(7)–Co–C(7′)	92.9 (3)
C(1)–Co–B(2′)	127.7 (3)	B(8)–Co–B(10′)	130.0 (4)	C(1)–Co–B(6′)	96.5 (3)	B(7)–Co–B(2′)	93.2 (4)
C(2)–Co–C(7′)	127.1 (3)	B(8)–Co–B(2′)	130.3 (4)	C(2)–Co–B(2′)	94.3 (4)	B(8)–Co–C(7′)	99.3 (4)
C(2)–Co–B(10′)	133.4 (3)	B(4)–Co–C(7′)	135.0 (3)	C(2)–Co–B(6′)	98.6 (3)	B(4)–Co–B(10′)	95.8 (4)
(B) Angles around Triangular Faces							
C–Co–C							
C(1)–Co–C(2)	45.7 (3)						
C–Co–B							
C(1)–Co–B(4)	49.4 (3)	C(7′)–Co–B(2′)	47.7 (3)	C(2)–Co–B(7)	47.3 (3)		
B–Co–B							
B(4)–Co–B(8)	49.6 (4)	B(2′)–Co–B(6′)	50.7 (4)	B(7)–Co–B(8)	49.9 (4)	B(6′)–Co–B(10′)	48.2 (4)
Co–C–C							
Co–C(1)–C(2)	67.1 (4)			Co–C(2)–C(1)	67.2 (4)		
Co–C–B							
Co–C(1)–B(4)	66.4 (4)	Co–C(7′)–B(2′)	68.3 (4)	Co–C(2)–B(7)	66.3 (4)		
Co–B–C							
Co–B(4)–C(1)	64.3 (4)	Co–B(2′)–C(7′)	64.0 (4)	Co–B(7)–C(2)	66.4 (4)		
Co–B–B							
Co–B(4)–B(8)	65.7 (4)	Co–B(2′)–B(6′)	65.9 (4)	Co–B(8)–B(4)	64.7 (4)	Co–B(6′)–B(2′)	63.4 (4)
Co–B(7)–B(8)	66.7 (4)	Co–B(10′)–B(6′)	64.0 (4)	Co–B(8)–B(7)	63.4 (4)	Co–B(6′)–B(10′)	67.8 (4)
C–C–B							
C(2)–C(1)–B(6)	61.2 (6)	C(8′)–C(7′)–B(3′)	65.8 (6)	C(1)–C(2)–B(6)	63.5 (6)	C(7′)–C(8′)–B(3′)	61.9 (6)
C–B–C							
C(1)–B(6)–C(2)	55.4 (5)	C(7′)–B(3′)–C(8′)	52.3 (5)				
B–C–B							
B(4)–C(1)–B(5)	62.0 (5)	B(2′)–C(7′)–B(3′)	63.1 (6)	B(6)–C(2)–B(11)	61.6 (6)	B(9′)–C(8′)–B(4′)	63.5 (6)
B(5)–C(1)–B(6)	61.1 (6)	B(3′)–C(8′)–B(4′)	60.2 (6)	B(7)–C(2)–B(11)	63.1 (6)		
B–B–C							
B(5)–B(4)–C(1)	58.0 (5)	B(2′)–B(3′)–C(7′)	57.9 (5)	B(11)–B(6)–C(2)	58.5 (6)	B(3′)–B(4′)–C(8′)	59.0 (5)
B(4)–B(5)–C(1)	60.0 (5)	B(3′)–B(2′)–C(7′)	59.0 (5)	B(11)–B(7)–C(2)	59.2 (5)	B(9′)–B(4′)–C(8′)	53.7 (5)
B(6)–B(5)–C(1)	60.6 (6)	B(4′)–B(3′)–C(8′)	60.8 (5)	B(6)–B(11)–C(2)	59.9 (6)		
B(5)–B(6)–C(1)	58.4 (6)	B(4′)–B(9′)–C(8′)	62.8 (5)	B(7)–B(11)–C(2)	57.7 (5)		
B–B–B							
B(5)–B(4)–B(9)	59.6 (6)	B(3′)–B(2′)–B(1′)	60.4 (6)	B(8)–B(9)–B(12)	60.1 (6)	B(4′)–B(1′)–B(5′)	59.2 (6)
B(8)–B(4)–B(9)	60.5 (6)	B(6′)–B(2′)–B(1′)	60.9 (6)	B(10)–B(9)–B(12)	59.2 (6)	B(3′)–B(4′)–B(1′)	59.8 (6)
B(4)–B(5)–B(9)	60.9 (6)	B(2′)–B(3′)–B(1′)	59.6 (6)	B(5)–B(10)–B(6)	59.2 (6)	B(9′)–B(4′)–B(5′)	59.4 (5)
B(6)–B(5)–B(10)	59.2 (6)	B(1′)–B(3′)–B(4′)	60.4 (6)	B(5)–B(10)–B(9)	59.8 (6)	B(1′)–B(4′)–B(5′)	60.6 (6)
B(9)–B(5)–B(10)	59.3 (6)	B(10′)–B(9′)–B(5′)	60.2 (5)	B(6)–B(10)–B(11)	59.5 (6)	B(9′)–B(5′)–B(10′)	59.4 (5)
B(5)–B(6)–B(10)	61.6 (6)	B(4′)–B(9′)–B(5′)	59.4 (6)	B(9)–B(10)–B(12)	60.6 (6)	B(9′)–B(5′)–B(4′)	61.2 (5)
B(10)–B(6)–B(11)	60.2 (6)	B(9′)–B(10′)–B(5′)	60.4 (6)	B(11)–B(10)–B(12)	60.1 (6)	B(10′)–B(5′)–B(6′)	60.2 (6)
B(8)–B(7)–B(12)	61.4 (6)	B(6′)–B(10′)–B(5′)	60.7 (6)	B(6)–B(11)–B(10)	60.3 (6)	B(6′)–B(5′)–B(1′)	60.9 (6)
B(11)–B(7)–B(12)	60.3 (6)	B(2′)–B(6′)–B(1′)	57.8 (6)	B(7)–B(11)–B(12)	59.5 (6)	B(1′)–B(5′)–B(4′)	60.3 (6)
B(4)–B(8)–B(9)	60.5 (6)	B(10′)–B(6′)–B(5′)	59.0 (5)	B(10)–B(11)–B(12)	59.9 (6)		
B(7)–B(8)–B(12)	58.5 (5)	B(1′)–B(6′)–B(5′)	59.5 (6)	B(7)–B(12)–B(8)	60.1 (5)		
B(9)–B(8)–B(12)	59.3 (6)	B(2′)–B(1′)–B(3′)	60.0 (6)	B(7)–B(12)–B(11)	60.2 (6)		
B(4)–B(9)–B(5)	59.6 (6)	B(2′)–B(1′)–B(6′)	61.3 (6)	B(8)–B(12)–B(9)	60.7 (6)		
B(4)–B(9)–B(8)	59.0 (5)	B(3′)–B(1′)–B(4′)	59.8 (6)	B(9)–B(12)–B(10)	60.3 (6)		
B(5)–B(9)–B(10)	61.0 (6)	B(6′)–B(1′)–B(5′)	59.6 (6)	B(10)–B(12)–B(11)	60.1 (6)		
(C) Angles around Pentagonal Faces							
C–Co–B							
C(1)–Co–B(7)	81.5 (4)	C(7′)–Co–B(10′)	86.4 (4)	C(2)–Co–B(4)	82.2 (4)		
C(1)–Co–B(8)	83.9 (4)	C(7′)–Co–B(6′)	83.9 (3)	C(2)–Co–B(8)	82.9 (3)		
B–Co–B							
B(4)–Co–B(7)	84.5 (4)	B(2′)–Co–B(10′)	86.5 (4)				
C–C–Co							
		C(8′)–C(7′)–Co	116.6 (5)				
B–C–Co							
B(5)–C(1)–Co	122.7 (5)	B(3′)–C(7′)–Co	125.9 (6)	B(11)–C(2)–Co	124.8 (5)		
B(6)–C(1)–Co	123.8 (6)			B(6)–C(2)–Co	126.0 (6)		

Table Va (*Continued*)

Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg	Atoms 1, 2, 3	Angle, deg
B-B-Co							
B(5)-B(4)-Co	117.3 (6)	B(3′)-B(2′)-Co	118.3 (6)	B(12)-B(7)-Co	121.6 (6)	B(5′)-B(10′)-Co	114.7 (6)
B(9)-B(4)-Co	118.8 (6)	B(1′)-B(2′)-Co	119.6 (6)	B(9)-B(8)-Co	117.9 (6)	B(1′)-B(6′)-Co	114.8 (6)
B(11)-B(7)-Co	121.4 (6)	B(9′)-B(10′)-Co	107.2 (6)	B(12)-B(8)-Co	116.1 (5)	B(5′)-B(6′)-Co	116.5 (5)
C-C-B							
C(2)-C(1)-B(4)	109.8 (6)	C(8′)-C(7′)-B(2′)	112.8 (6)	C(1)-C(2)-B(7)	111.4 (6)	C(7′)-C(8′)-B(4′)	111.9 (6)
C(2)-C(1)-B(5)	109.3 (7)	C(7′)-C(8′)-B(9′)	116.3 (7)	C(1)-C(2)-B(11)	113.2 (7)		
B-C-B							
B(4)-C(1)-B(6)	112.3 (6)	B(3′)-C(8′)-B(9′)	114.3 (6)	B(6)-C(2)-B(7)	113.5 (6)		
B-B-C							
B(8)-B(4)-C(1)	105.7 (6)	B(6′)-B(2′)-C(7′)	106.2 (6)	B(5)-B(6)-C(2)	102.5 (7)	B(10′)-B(9′)-C(8′)	110.3 (7)
B(9)-B(4)-C(1)	104.4 (7)	B(1′)-B(2′)-C(7′)	105.8 (7)	B(10)-B(6)-C(2)	104.4 (7)	B(5′)-B(9′)-C(8′)	107.4 (7)
B(9)-B(5)-C(1)	106.9 (7)	B(1′)-B(3′)-C(7′)	104.4 (7)	B(8)-B(7)-C(2)	108.1 (7)	B(1′)-B(4′)-C(8′)	101.5 (7)
B(10)-B(5)-C(1)	105.9 (7)	B(4′)-B(3′)-C(7′)	104.5 (7)	B(12)-B(7)-C(2)	106.3 (7)	B(5′)-B(4′)-C(8′)	100.4 (7)
B(10)-B(6)-C(1)	106.1 (7)	B(2′)-B(3′)-C(8′)	98.5 (7)	B(10)-B(11)-C(2)	105.6 (7)		
B(11)-B(6)-C(1)	104.1 (7)	B(1′)-B(3′)-C(8′)	103.2 (7)	B(12)-B(11)-C(2)	104.4 (7)		
B-B-B							
B(5)-B(4)-B(8)	108.1 (7)	B(3′)-B(2′)-B(6′)	109.5 (7)	B(5)-B(10)-B(11)	106.0 (7)	B(9′)-B(4′)-B(1′)	105.5 (7)
B(4)-B(5)-B(6)	110.3 (7)	B(2′)-B(3′)-B(4′)	107.4 (7)	B(5)-B(10)-B(12)	106.8 (8)	B(9′)-B(5′)-B(6′)	104.5 (6)
B(4)-B(5)-B(10)	108.3 (7)	B(10′)-B(9′)-B(4′)	111.5 (7)	B(6)-B(10)-B(9)	108.5 (8)	B(9′)-B(5′)-B(1′)	106.6 (7)
B(6)-B(5)-B(9)	108.0 (7)	B(9′)-B(10′)-B(6′)	105.6 (7)	B(6)-B(10)-B(12)	107.8 (8)	B(10′)-B(5′)-B(1′)	111.0 (7)
B(5)-B(6)-B(11)	108.5 (7)	B(2′)-B(6′)-B(10′)	110.5 (6)	B(9)-B(10)-B(11)	108.6 (8)	B(10′)-B(5′)-B(4′)	112.3 (7)
B(8)-B(7)-B(11)	110.8 (7)	B(2′)-B(6′)-B(5′)	105.0 (7)	B(6)-B(11)-B(7)	107.8 (7)	B(6′)-B(5′)-B(4′)	109.4 (7)
B(4)-B(8)-B(7)	104.9 (6)	B(10′)-B(6′)-B(1′)	108.8 (7)	B(6)-B(11)-B(12)	108.4 (7)		
B(4)-B(8)-B(12)	107.0 (7)	B(2′)-B(1′)-B(4′)	107.2 (6)	B(7)-B(11)-B(10)	107.1 (7)		
B(7)-B(8)-B(9)	105.1 (7)	B(2′)-B(1′)-B(5′)	107.8 (7)	B(7)-B(12)-B(9)	107.5 (7)		
B(4)-B(9)-B(10)	108.6 (6)	B(3′)-B(1′)-B(6′)	109.5 (7)	B(7)-B(12)-B(10)	107.9 (7)		
B(4)-B(9)-B(12)	106.4 (7)	B(3′)-B(1′)-B(5′)	107.6 (7)	B(8)-B(12)-B(10)	109.7 (8)		
B(5)-B(9)-B(8)	106.9 (6)	B(6′)-B(1′)-B(4′)	107.5 (7)	B(8)-B(12)-B(11)	109.7 (7)		
B(5)-B(9)-B(12)	106.7 (6)	B(3′)-B(4′)-B(9′)	105.1 (7)	B(9)-B(12)-B(11)	108.4 (7)		
B(8)-B(9)-B(10)	108.4 (7)	B(3′)-B(4′)-B(5′)	108.7 (8)				
(D) Angles between Pyridine N and B_8C_2 Ligand							
py(N)-B(9′)-C(8′)	120.8 (7)	py(N)-B(9′)-B(4′)	114.2 (7)	py(N)-B(9′)-B(10′)	122.3 (7)	py(N)-B(9′)-B(5′)	120.5 (7)
(E) Angles within the Pyridine Ring							
py(1)-py(N)-py(5)	119.2 (7)	py(2)-py(3)-py(4)	118.6 (9)	py(1)-py(2)-py(3)	119.9 (8)	py(4)-py(5)-py(N)	123.0 (8)
py(N)-py(1)-py(2)	121.0 (8)	py(3)-py(4)-py(5)	118.2 (8)				
(II) Angles within the $(C_2H_5)_4N^+$ Cation							
(A) Carbon-Nitrogen-Carbon Angles							
Et(1a)-N-Et(2a)	109.9 (6)	Et(2a)-N-Et(3a)	107.3 (6)	Et(1a)-N-Et(4a)	106.4 (7)	Et(3a)-N-Et(4a)	110.8 (6)
Et(1a)-N-Et(3a)	110.7 (6)	Et(2a)-N-Et(4a)	111.9 (6)				
(B) Nitrogen-Carbon-Carbon Angles							
N-Et(1a)-Et(1b)	116.1 (8)	N-Et(3a)-Et(3b)	116.9 (8)	N-Et(2a)-Et(2b)	117.7 (7)	N-Et(4a)-Et(4b)	114.4 (8)

[a] See footnote *a* of Table IVa.

onal bonding face of the B_9C_2 ligand, to attain an 18 outer electron (Kr) configuration.

It should be noted that the present compound represents the first reported example of a transition metal complex with a *π-mono*dentate B_8C_2 ligand.

To simplify discussion of the overall molecular structure, the equatorial pentagonal belts of the carborane ligands have been defined as α and α′ (directly bonded to the cobalt atom) and β and β′ (the "second level")—see Table VI. Root-mean-square deviations from the least-squares planes are 0.011 Å (α), 0.029 Å (β), 0.003 Å (α′), and 0.054 Å (β′).

The unprimed (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand shows no major distortions from the idealized geometry of an 11-particle icosahedral fragment. Thus both α and β planes *are planar* within the limits of experimental error and the α-β interplanar angle is only 1° 31′. Similarly, bond distances and angles are consistent with values from other regular icosahedral metallocarboranes.[3-5,20-27] [Bonds in the present system have the following ranges in length: C-C = 1.598 (13), B-C = 1.651 (12)-1.739 (14), B-B = 1.730 (16)-1.790 (15) Å.]

The primed [(11′)-7′,8′-$B_8C_2H_{10}py^{2-}$] ligand is, however, significantly distorted from an idealized icosahedral geometry. In particular, the β′ system [defined by C(8′), B(3′), B(1′), B(5′), B(9′)] is decidedly nonplanar, with atoms C(8′), B(3′), and B(1′) each deviating from the "least-squares plane" by more than three standard deviations. In addition, the dihedral angle between the α′ belt (which *is* planar within experimental error) and the β′ system is 6° 21′.

The nature of the distortion of the β′ system is revealed by defining a further plane (β″) through atoms B(5′), B(1′), and B(3′). One now discovers that both C(8′) and B(9′) are significantly displaced below β″ (*i.e.*, toward the α′ plane) by 0.253 (8) and 0.139 (11) Å, respectively. The most obvious effect (or, perhaps, cause!) of this distortion is the abnormally short C(7′)-C(8′) distance of 1.504 (12) Å—which is in very sharp contrast to the value of 1.717 (5) Å for the similarly situated C(1′)-C(2′) bond in (3,4′)-[$(CH_3)_2B_9C_2H_9]_2$-Ni^{IV}.[27] The wide ranges of values for similar types of bonds (especially C-B) within the B_8C_2 skeleton is another reflection of the distortions and irregularities within this species [*i.e.*, C-B = 1.600 (12)-1.765 (14), B-B = 1.727 (14)-1.802 (14) Å]. Interatomic angles show similar variations consistent with these distortions; the reader is referred to Table Va for a listing of individual values.

Table Vb. Average Bond Angles in the Molecule

Atoms	No. of angles	Range,[a] deg	Av,[b] deg
(A) Angles around All Triangular Faces			
C–Co–C	1	45.7 (3)	45.7
C–Co–B	3	47.3 (3)–49.4 (3)	47.9 (1.1)
B–Co–B	4	48.2 (4)–50.7 (4)	49.6 (1.0)
Co–C–C	2	67.1 (4)–67.2 (4)	67.2 (0.1)
Co–C–B	3	66.3 (4)–68.3 (4)	67.0 (1.1)
Co–B–C	3	64.0 (4)–66.4 (4)	64.9 (0.8)
Co–B–B	8	63.4 (4)–67.8 (4)	65.2 (1.6)
C–C–B	4	61.2 (6)–65.8 (6)	63.1 (2.0)
C–B–C	2	52.3 (5)–55.4 (5)	53.9 (2.2)
B–C–B	7	60.2 (6)–63.5 (6)	62.1 (1.2)
B–B–C	14	53.7 (5)–62.8 (5)	59.0 (2.0)
B–B–B	54	57.8 (6)–61.6 (6)	60.0 (0.7)
	105		
(B) Angles around All Pentagonal Faces			
C–Co–B	6	81.5 (4)–86.4 (4)	83.5 (1.7)
B–Co–B	2	84.5 (4)–86.5 (4)	85.5 (1.4)
C–C–Co	1	116.6 (5)	116.6
B–C–Co	5	122.7 (5)–126.0 (6)	124.8 (1.3)
B–B–Co	12	107.2 (6)–121.6 (6)	117.0 (3.8)
C–C–B	7	109.3 (7)–116.3 (7)	112.1 (2.3)
B–C–B	3	112.3 (6)–114.3 (6)	113.4 (1.0)
B–B–C	22	98.5 (7)–110.3 (7)	104.8 (2.6)
B–B–B	47	104.5 (6)–112.3 (7)	107.9 (1.8)
	105		
(C) Angles between py(N) and B_8C_2 Ligand			
py(N)–B–B	3	114.2 (7)–122.3 (7)	119.0 (4.2)
py(N)–B–C	1	120.8 (7)	120.8
(D) Angles within Pyridine Ring			
C–N–C	1	119.2 (7)	119.2
N–C–C	2	121.0 (8)–123.0 (8)	122.0 (1.4)
C–C–C	3	118.2 (8)–119.9 (8)	118.9 (0.9)
(E) Angles within Tetraethylammonium Cation			
C–N–C	6	106.4 (7)–111.9 (6)	109.5 (2.2)
N–C–C	4	114.4 (8)–117.7 (7)	116.3 (1.4)

[a] Esd's for the individual angles 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 IVb.

Table VI. Important Planes[a] in the Molecule

Atom	Dev, A	Atom	Dev, A
α Plane: C(1), C(2), B(4), B(7), B(8)			
$+0.9491X + 0.2990Y + 0.0993Z = +5.886$			
C(1)	−0.004 (8)	B(7)	−0.014 (10)
C(2)	+0.012 (8)	B(8)	+0.011 (11)
B(4)	−0.005 (10)	Co	−1.488 (3)
β Plane: B(5), B(6), B(9), B(11), B(12)			
$+0.9558X + 0.2730Y + 0.1062Z = +7.352$			
B(5)	−0.030 (11)	B(11)	−0.010 (9)
B(6)	+0.025 (11)	B(12)	−0.009 (9)
B(9)	+0.023 (10)	Co	−2.972 (3)
α′ Plane: C(7′), B(2′), B(10′), B(6′)			
$+0.9591X + 0.2819Y + 0.0249Z = +2.695$			
C(7′)	−0.002 (8)	B(6′)	−0.003 (9)
B(2′)	+0.004 (11)	Co	+1.471 (3)
B(10′)	+0.002 (10)		
β′ Plane: C(8′), B(3′), B(9′), B(1′), B(5′)			
$+0.9842X + 0.1763Y + 0.0186Z = +1.114$			
C(8′)	+0.059 (8)	B(1′)	+0.049 (11)
B(3′)	−0.065 (10)	B(5′)	−0.018 (11)
B(9′)	−0.026 (11)	Co	+2.854 (3)
β″ Plane: B(3′), B(1′), B(5′)			
$+0.9647X + 0.2632Y + 0.0088Z = +1.141$			
C(8′)	+0.253 (8)	B(9′)	+0.139 (11)
Pyridine plane: py(N), py(1), py(2), py(3), py(4), py(5)			
$+0.7738X + 0.5540Y - 0.3070Z = +1.308$			
py(N)	−0.006 (5)	py(4)	−0.015 (5)
py(1)	−0.000 (6)	py(5)	+0.014 (6)
py(2)	−0.001 (5)	B(9′)	+0.062 (11)
py(3)	+0.008 (5)		

Dihedral Angles

α–β = 1° 31′

α′–β′ = 6° 21′

β–β′ = 7° 41′

α–α′ = 4° 22′

α′–β″ = 4° 8′

β′–pyridine = 31° 24′

α–β′ = 8° 39′

α′–β = 4° 42′

[a] 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 $Z = zc \sin\beta$.

Table VII. Intermolecular Contacts

Old atom	New atom	New atom transformation	Distance, A
(A) B· · ·H and C· · ·H Contacts (to 3.0 A)			
B(8)	H(py3)	$-x, -y+1, -z$	2.95
B(8)	H4a(1)	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$	2.90
B(12)	H4b(1)	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$	2.92
B(1′)	H(py1)	$-x, y+\frac{1}{2}, -z+\frac{1}{2}$	2.98
B(3′)	H(py1)	$-x, y+\frac{1}{2}, -z+\frac{1}{2}$	2.87
py(1)	H(3′)	$-x, y-\frac{1}{2}, -z+\frac{1}{2}$	2.99
(B) H· · ·H Contacts (to 2.5 A)			
H(1)	H2b(2)	$-x+1, -y, -z$	2.41
H(5)	H3b(1)	$-x+1, -y+1, -z$	2.40
H(8)	H(py3)	$-x, -y+1, -z$	2.36
H(8)	H4a(1)	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$	2.41
H(8)	H2b(3)	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$	2.49
H(12)	H4a(1)	$-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$	2.39
H(1′)	H(8′)	$-x, y+\frac{1}{2}, -z+\frac{1}{2}$	2.47
H(1′)	H(py1)	$-x, y+\frac{1}{2}, -z+\frac{1}{2}$	2.37
H(2′)	H4a(2)	$-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$	2.48
H(3′)	H(py1)	$-x, y+\frac{1}{2}, -z+\frac{1}{2}$	2.31
H(5′)	H(5′)	$-x, -y, -z$	2.43
H(5′)	H(py5)	$-x, -y, -z$	2.43

The present analysis has failed, however, to reveal one very important feature of the $B_8C_2H_{10}py^{2-}$ ligand, and that is the site of the "extra" hydrogen atom. Since the pyridine substituent on B(9′) is not significantly displaced from the terminal position of idealized icosahedral geometry [py(N)-B(9′)-C(8′) = 120.8 (7)°, py(N)-B(9′)-B(10′) = 122.3 (7)°, py(N)-B(9′)-B(4′) = 114.2 (7)°, py(N)-B(9′)-B(5′) = 120.5°; average 119.5°] and since the terminal hydrogens have been unambiguously located for each of the nine remaining cage atoms, the tenth or "unaccounted-for" hydrogen must, therefore, occupy some bridging position around the cage. This hydrogen atom is, most probably, associated in some way with the open pentagonal C(8′)-C(7′)-Co-B(10′)-B(9′) face, as is the "extra" hydrogen of the $B_9C_2H_{12}^-$ ion.[28] Specific possibilities include (i) a B(9′)-H-B(10′) bridge, (ii) a B(9′)-H-C(8′) bridge, and (iii) a C(8′)-H-C(7′) bridge. In the absence of any known examples of B-H-C or C-H-C bridges, we favor possibility (i). We may note, also that a broad peak in the ^{1}H nmr spectrum of this molecule, at +9.2 ppm from tetramethylsilane, has been attributed[7] to a proton in a B-H-B bridge.

It is unfortunate that both "observed" and "difference" Fourier syntheses, both before and after refinement of anisotropic thermal parameters, failed to reveal the position of this hydrogen atom.

Within the $[(B_9C_2H_{11})Co(B_8C_2H_{10}py)^-]$ anion *as a whole* there is a dihedral angle of 4° 22′ between the α and α′ bonding faces of the constituent carborane dianions, indicating that the two ligands are nonparallel. [Further evidence is the B(10)· · ·Co· · ·B(4′) angle of 174.3 (3)°.] The direction of this interligand tilting can be discerned from examination of the interannular contacts between the α and α′ planes. In

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(28) M. F. Hawthorne, *Accounts Chem. Res.*, 1, 281 (1968).

particular, the shortest contact, B(7)· · ·C(7′) = 2.949 (12) Å, is directly opposite the contact of maximum distance, C(1)· · ·B(10′) = 3.240 (14) Å.

Similar distortions in (3,4′)-[$(CH_3)_2B_9C_2H_9]_2Ni^{IV}$ [23] (α-α′ = 14° 51′) and [$Co(B_9C_2H_8Br_3)_2^-$][23] (α-α′ = *ca.* 3°) have been attributed to steric effects arising from repulsive interactions between α and α′ substituent groups. In the present case, however, both α and α′ are unsubstituted and the dihedral angle of 4° 22′ between these planes may well be the result of electronic effects.

Distances between the cobalt atom and the α and α′ planes are respectively 1.488 (3) and 1.471 (3) Å. Bonding between the cobalt and the α plane is essentially symmetrical, the shortest bonding distance being Co-B(7) = 2.056 (10) Å and the longest being Co-B(8) = 2.111 (9) Å. Distances from the cobalt to atoms of the α′ plane, however, vary quite significantly and range from 2.014 (8) Å for Co-C(7′) to 2.191 (10) Å for Co-B(10′). A similar situation has been observed in (3,4′)-[$(CH_3)_2B_9C_2H_9]_2Ni^{IV}$.[27,29] In the present case, however, asymmetric bonding of the metal to the B_8C_2 ligand may well be the *cause, rather than the result*, of the dihedral angle of 4° 22′.

The Pyridine Substituent. The pyridine substituent on B(9′) approximates to pseudo-D_{6h} symmetry. Individual bond lengths within the ring are py(N)-py(1) = 1.335 (10) Å, py(N)-py(5) = 1.345 (11) Å, py(1)-py(2) = 1.372 (13) Å, py(2)-py(3) = 1.387 (14) Å, py(3)-py(4) = 1.388 (13) Å, py(4)-py(5) = 1.360 (13) Å. Individual bond angles range from py(3)-py(4)-py(5) = 118.2 (8)° to py(4)-py(5)-py(N) = 123.0 (8)° and average 120.0°.

The position of the pyridine ring is not significantly displaced from that calculated assuming idealized icosahedral geometry (*vide supra*). The py(N)-B(9′) distance of 1.592 (11) Å is consistent with the average B(sp^3)-N(sp^2) distance of 1.544 (21) Å in [$HB(C_3N_2H_3)_3]_2Co^{II}$[30] and with the average B(sp^3)-N(sp^3) distances of 1.59 (4) Å in [$HB(NH_3)_2]Cl$[31] and 1.56 (5) Å in $H_3B{\cdot}NH_3$.[32,33] It appears, therefore, that there is no significant delocalization of electron density between the aromatic B_8C_2 ligand and the pyridine ring (as would be evidenced by a decrease in the N-B bond length from the value of a normal B(sp^3)-N(sp^2) single bond).

The Tetraethylammonium Ion. The $(C_2H_5)_4N^+$ species shows no significant distortions from idealized D_{2d} symmetry, with coordination about the central nitrogen atom being essentially tetrahedral. Carbon-nitrogen-carbon angles vary from 106.4 (7) to 111.9 (6)° and average 109.5 (2.2)°. Carbon-carbon-nitrogen angles range from 114.4 (8) to 117.7 (7)°, averaging 116.3 (1.4)°. Average bond lengths within the $(C_2H_5)_4N^+$ ion are N-C = 1.514 (12) Å and C-C = 1.493 (38) Å.

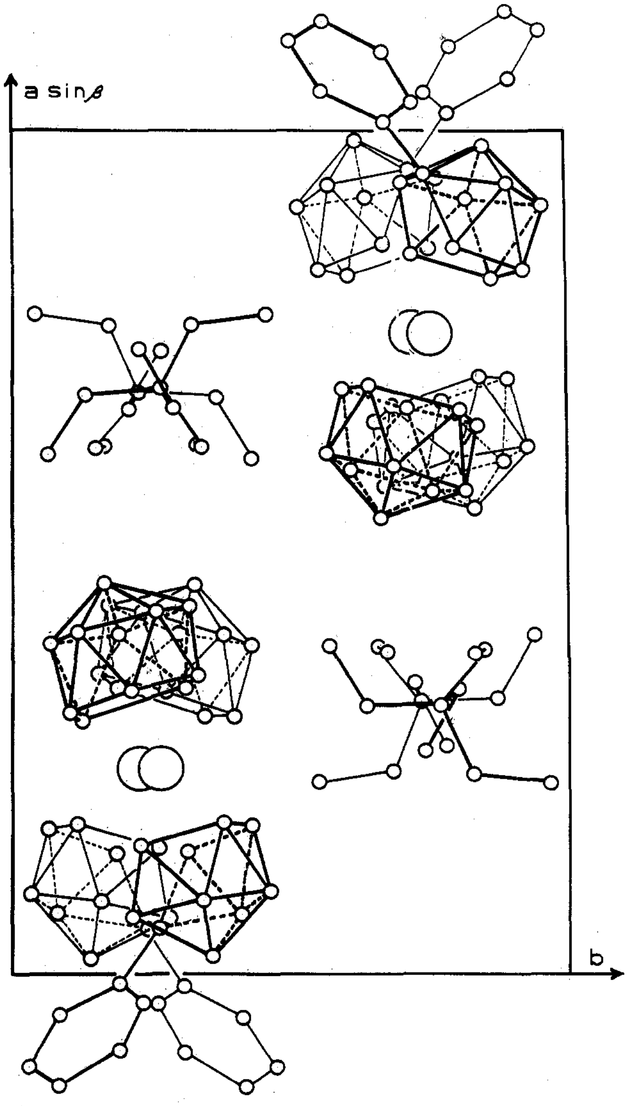

Figure 3. The packing of ions within the unit cell.

Intermolecular Contacts. Figure 3 shows the packing of [$(B_9C_2H_{11})Co^{III}(B_8C_2H_{10}py)^-][(C_2H_5)_4N^+]$ molecules within the unit cell, viewed down *c*. The individual ions are separated by normal van der Waals distances. Quantitative data on intermolecular contacts are listed in Table VII. Shortest contacts of each type are boron· · ·hydrogen = 2.87 Å, ethyl carbon· · ·hydrogen = 3.10 Å, pyridine carbon· · ·hydrogen = 2.99 Å, and hydrogen· · ·hydrogen = 2.31 Å.

Registry No. [$(C_2H_5)_4N]\{(B_9C_2H_{11})Co[(B_8C_2H_{10})C_5H_5N]\}$, 38637-44-4.

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(29) The situations are *not identical*, however, since in the Ni(IV) complex, the metal is bonded asymmetrically to the (3)-1,2-dicarbollide ligand, containing both carbon atoms in the bonding face. This may constitute further evidence of electronic *vs.* steric effects.

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