hydrogen, ammonia, or azide, or a mixture of any or all of these.[24] In the presence of transition metals, hydrazine yields nitrogen and hydrogen by a process which is essentially catalytic. For these reasons the mechanism of formation of $[Ru(NH_3)_5N_2]^{2+}$ is difficult to elucidate. A complete study of the reaction is in progress, and it is hoped that a more definite conclusion will be reached. At present it appears that when ruthenium(IV) is present the reaction proceeds *via* coordinated azide, this mechanism accounting for the band at 2090 cm⁻¹. In view of the results obtained with $[Ru^{III}(NH_3)_5H_2O]^{3+}$ and NaN_3 it would appear that the intermediate in the reaction is a $Ru^{III}-N_3$ species, the N_3^- being produced from hydrazine by reduction of Ru^{IV} to Ru^{III}. The reaction between $[Ru^{III}(NH_3)_5H_2O]^{3+}$ and hydrazine may proceed *via* coordinated azide or *via* some other adduct which decomposes to leave a bonded nitrogen molecule. No intermediate can be detected at present and hence

no path can be suggested for this reaction. We have attempted to prepare $[Ru(NH_5)_5N_2]^{2+}$ from various ruthenium ammines and nitrogen gas under pressure. All such attempts have failed. The preparation of $[Ru^{II}(NH_3)_5N_2]^{2+}$ from $[Ru^{III}(NH_3)_5Cl]^{2+}$ using nitrogen and amalgamated zinc has recently been reported,[20] and Chatt has reported the formation of the same compound from the reaction of hydrazine and $(PR_3P)_3RuCl_3$.[25]

(24) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 6.

(25) J. Chatt, G. J. Leigh, and R. J. Paske, Chemical Society Autumn Meeting, Sussex, Sept 1966.

The Crystal and Molecular Structure of Tetraethylammonium Bis-(3)-1,2-dicarbollylcuprate(II)[1]

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Abstract: The crystal structure of $(Et_4N)_2Cu(C_2B_9H_{11})_2$ has been determined from a single-crystal X-ray diffraction study. The two carbons of the icosahedral fragment were distinguished unambiguously from the borons. The coordination about copper deviates from the usual π-sandwich configuration by a slippage of the carborane moieties parallel to one another so that the primary coordination sphere of copper is six borons, three from each carborane cage ($\overline{Cu-C}$ = 2.57 A, $\overline{Cu-B}$ = 2.20 A). Although only the center is required crystallographically, the anion's molecular symmetry is within experimental error C_{2h}.

During the past 2 years Hawthorne[2-7] and coworkers have synthesized several carborane derivatives of transition metals. X-Ray crystal structure studies by Zalkin,[8,9] *et al.*, confirmed the π-sandwich structure postulated by Hawthorne for the iron and rhenium dicarbollyl derivatives. More recently Hawthorne and Warren[10] isolated a blue crystalline compound of copper from an aqueous, strongly basic solution of cupric chloride and (3)-1,2-dicarbollide anion.

In view of the fact that organocopper chemistry is very sparse and representative compounds, apart from the acetylides and olefins, are very unstable, the new carbametallic of copper is very unusual in its stability. There seems to be no analogous chemistry of copper, the only cyclopentadienide being triethylphosphinecyclopentadienylcopper $[C_5H_5CuPEt_3]$ which has been reported to be a σ complex.[11] To our knowledge no organometallic compounds of copper(II) have been reported.

Experimental Section

Dark royal blue platelets of the tetraethylammonium salt of $Cu(C_2B_9H_{11})_2^{2-}$ were kindly provided by Professor M. F. Hawthorne of this department. A single crystal 0.66 × 0.46 × 0.25 mm was selected using a polarizing microscope and mounted in a borosilicate capillary. The crystals are strongly dichroic. When viewed in transmission with polarized light propagating parallel to a^*, the crystals are blue if the electric vector is approximately parallel to

(1) Supported by an intramural grant of the University of California.

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(6) P. A. Wegner and M. F. Hawthorne, *ibid.*, 861 (1966).

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

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(9) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, 5, 1189 (1966).

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(11) (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 2, 32 (1956); (b) G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, 89, 2855 (1967).

Table I. Final Positional Parameters[a,b] in $(Et_4N)_2Cu(C_2B_9H_{11})_2$

Atom	x/a	y/b	z/c	X^c	Y	Z
Cu	0.0	0.0	0.0	0.0	0.0	0.0
			Cage Atoms			
CB(2)	0.0587	−0.0522	0.2665	0.61	−0.96	2.32
CB(3)	0.0804	0.1287	0.2712	0.86	0.55	2.36
B(4)	0.1471	0.2187	0.1146	1.67	1.06	1.00
B(5)	0.1810	0.0720	−0.0013	2.09	−0.42	−0.01
B(6)	0.1061	−0.1097	0.1022	1.20	−1.68	0.89
B(7)	0.1631	0.0821	0.4012	1.78	−0.43	3.49
B(8)	0.2238	0.2635	0.2975	2.51	0.91	2.59
B(9)	0.2883	0.2209	0.1296	3.30	0.23	1.13
B(10)	0.2635	0.0151	0.1214	3.01	−1.48	1.06
B(11)	0.1829	−0.0714	0.2859	2.04	−1.88	2.49
B(12)	0.2949	0.1341	0.3033	3.33	−0.69	2.64
H(2)	−0.02	−0.13	0.33	−0.32	−1.24	2.87
H(3)	0.02	0.17	0.33	0.14	1.25	2.87
H(4)	0.15	0.30	0.06	1.72	1.81	0.52
H(5)	0.19	0.05	−0.13	2.23	−0.60	−1.13
H(6)	0.08	−0.23	0.03	0.92	−2.58	0.29
H(7)	0.15	0.08	0.52	1.59	−0.44	4.52
H(8)	0.26	0.39	0.36	2.85	1.84	3.13
H(9)	0.36	0.30	0.07	4.14	0.56	0.61
H(10)	0.34	−0.01	0.07	3.91	−2.14	0.61
H(11)	0.18	−0.17	0.34	1.98	−2.44	3.22
H(12)	0.38	0.15	0.37	4.29	−1.08	3.22
			Tetraethylammonium Group			
N	0.6996	0.3626	0.2307	8.02	−0.96	2.01
C(1)	0.5998	0.2585	0.1106	6.90	−1.26	0.96
C(2)	0.6612	0.2771	0.3831	7.54	−1.59	3.33
C(3)	0.8121	0.3581	0.1720	9.34	−1.64	1.49
C(4)	0.7197	0.5392	0.2546	8.25	0.51	2.21
C(5)	0.6199	0.3279	−0.0504	7.18	−0.66	−0.44
C(6)	0.6420	0.1005	0.3769	7.32	−3.08	3.28
C(7)	0.9149	0.4328	0.2929	10.50	−1.63	2.55
C(8)	0.6129	0.5708	0.2953	7.00	1.41	2.57

[a] The hydrogen atom positions were not refined. [b] $\sigma_x \simeq 0.0006$, $\sigma_y \simeq 0.0010$, $\sigma_z \simeq 0.0009$. [c] Y parallel to b, X in the a,b plane, Z perpendicular to X,Y.

c (10° deviation) and clear when the electric vector is oriented 10° from b.

Precession and Weissenberg photographs indicated that the crystal was triclinic, $a_0 = 12.98 \pm 0.01$ A, $b_0 = 9.09 \pm 0.01$ A, $c_0 = 8.73 \pm 0.01$ A, $\alpha = 93.5 \pm 0.1°$, $\beta = 90.1 \pm 0.1°$, $\gamma = 117.1 \pm 0.1°$. Cu Kα Weissenberg photos were used to measure a_0 and c_0; the other parameters were measured using a precession camera and Mo Kα radiation. Delaunay reduction indicated no simpler choice of cells.

Since no chemical analysis was available, an X-ray molecular weight was computed assuming one formula unit per cent cell. The results, 614 amu, indicated $(Et_4N)_2Cu(C_2B_9H_{11})_2$, molecular weight of 611 amu, as the most reasonable composition.

Reflections were collected for $h0l$ through $h6l$ out to $\sin\theta = 0.9$ on a Nonius integrating Weissenberg camera, using a multiple-film technique. Their intensities were estimated by comparison with a set of timed exposures of a single reflection from the same crystal. Cu Kα radiation was used and 2039 of 2470 accessible reflections were observed. The data were corrected for Lorentz polarization as well as absorption ($\mu r = 0.1$),[12] and the layers were placed on the same relative scale using data from a set of $hk0$ precession photographs.

All the calculations were performed on an IBM 7040 computer with a 32K memory. The block diagonal and full-matrix least-squares programs[13] as well as the Fourier program[14] were local modifications of those developed at the UCLA Crystallographic

Laboratories. The function of $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinement.

The atomic-scattering power of copper(I) was corrected for the real part of the anomalous dispersion by -2.0 e.[15] Scattering powers for neutral carbon, boron, nitrogen, and hydrogen were taken from standard tables.[16]

In the last six cycles of refinement the data were weighted as follows: $F_o \leq 12.5$, $w = 1.0$; $F_o > 12.5$, $w = 12.5/F_o$.[17]

Determination of Structure

With only one heavy atom per unit cell the structure was assumed to be centrosymmetric and a Fourier map was calculated based on all signs positive. The images of the 21 independent nonhydrogen atoms were clearly visible at this point.

Four cycles of block-diagonal and two cycles of full-matrix least-squares refinement of all positional and temperature factors (copper anisotropic and all cage atoms assumed to be boron) gave a residual of 0.14. Clear images of all eleven of the cage hydrogens as well as indications of the tetraethylammonium hydrogens were present in the difference Fourier.

At this point two factors made clear the choice of the two cage carbons. First the temperature factors

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(13) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, University of California at Los Angeles.
(14) P. Gantzel and H. Hope, unpublished.

(15) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 214, Table 3.3.2B.
(16) J. A. Ibers, ref 15, p 202, Table 3.3.1A.
(17) E. W. Hughes, J. Am. Chem. Soc., 63, 1737 (1941).

Table II. Anisotropic Temperature Parameters[a] in $(Et_4N)_2Cu(C_2B_9H_{11})_2$

	B_{11}[b,c]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2.73 (5)	2.24 (8)	3.86 (6)	2.32 (9)	−0.40 (8)	−0.28 (9)
CB(2)	3.1 (3)	2.3 (4)	4.5 (3)	2.7 (5)	0.4 (4)	0.0 (5)
CB(3)	3.4 (3)	3.5 (5)	4.1 (3)	3.5 (5)	1.0 (4)	−0.1 (5)
B(4)	3.4 (3)	3.0 (5)	4.2 (3)	2.9 (5)	−0.5 (5)	0.7 (5)
B(5)	2.8 (3)	3.1 (4)	3.9 (3)	2.5 (5)	0.3 (4)	−0.3 (5)
B(6)	3.5 (3)	4.3 (5)	4.0 (3)	3.7 (6)	−0.2 (5)	−1.0 (6)
B(7)	4.1 (3)	4.5 (5)	3.6 (3)	3.2 (6)	−0.8 (5)	0.6 (6)
B(8)	4.1 (3)	3.2 (5)	4.0 (3)	3.3 (6)	−0.2 (5)	−0.7 (5)
B(9)	3.3 (3)	2.2 (5)	4.4 (3)	3.1 (5)	−0.3 (5)	0.2 (5)
B(10)	3.3 (3)	3.5 (5)	4.7 (4)	3.5 (6)	0.3 (5)	0.0 (6)
B(11)	3.8 (3)	3.7 (5)	4.1 (3)	2.2 (6)	−0.2 (5)	1.7 (6)
B(12)	3.3 (3)	3.7 (5)	3.6 (3)	2.5 (5)	−1.0 (5)	−0.1 (5)
N	3.5 (2)	2.7 (4)	3.7 (2)	2.4 (4)	−0.2 (4)	−0.2 (4)
C(1)	4.2 (3)	4.0 (4)	4.4 (3)	3.3 (6)	−2.5 (5)	−1.4 (5)
C(2)	5.1 (4)	4.7 (6)	4.2 (3)	3.9 (6)	0.3 (5)	2.3 (6)
C(3)	3.7 (3)	5.2 (5)	6.2 (4)	4.7 (6)	0.5 (5)	0.0 (7)
C(4)	4.1 (3)	2.5 (5)	5.8 (4)	3.0 (5)	−0.3 (5)	−2.0 (6)
C(5)	8.1 (5)	4.0 (5)	4.7 (4)	5.4 (8)	−3.3 (7)	0.1 (6)
C(6)	7.5 (5)	5.3 (8)	7.9 (6)	3.7 (9)	−1.6 (9)	6.3 (9)
C(7)	3.8 (3)	6.4 (6)	8.1 (6)	4.6 (7)	−1.4 (7)	0.9 (9)
C(8)	5.4 (4)	4.3 (5)	6.9 (5)	6.0 (7)	−1.0 (6)	−2.5 (7)

[a] $Tr = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$. [b] Listing of $B_{ij} = 4b_{ij}/a^*_ia^*_j$ where a^*_i is the ith reciprocal lattice vector. Units are squared angstroms. [c] Estimated standard deviation of last significant figure in parentheses.

of two of the atoms were *ca.* 30% smaller than those of the other nine. Second the intracage atom–atom distances clearly factored into three classes, containing respectively 1 short, six medium, and 18 long bonds. These facts considered separately lead to identical choices for the two carbon atoms. From this point on these two atoms (CB(2) and CB(3)) were treated as carbons with the result that their refined temperature factors became consistent with the rest of the cage. The cage hydrogens were added but not refined, and two cycles of least-squares refinement on heavy-atom positional and temperature factors reduced the residual to 0.12. At this point the individual layers were rescaled, several key-punching blunders were corrected, and a decision was made to refine the tetraethylammonium (TEA) group anisotropically, neglecting the hydrogen atoms. Two more cycles then reduced the residual to 0.104. Finally the icosahedral cage along with the copper atom was allowed to refine anisotropically for two cycles. With all atoms anisotropic the cage and the tetraethylammonium groups had to be refined separately due to programming limitations. One cycle on TEA and one on the cage gave a final discrepancy factor of 0.091, based on observed reflections only. The coordinate shifts in the last two cycles of refinement were about 0.0001. The final atom parameters are given in Table I, and the anisotropic thermal parameters are given in Table II. Table III lists the observed and calculated structure factors. The estimated standard deviation of an observation of unit weight is 1.36 indicating that the weighting scheme was reasonably correct.

Discussion

The bond lengths and angles are listed in Tables IV and V. Standard deviations were estimated using Cruickshank's method.[18]

(18) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

The coordination about copper is that of a distorted π-sandwich compound as shown in Figure 1. The distortion from a π-sandwich structure can be visualized as having been effected by a slip of the dicarbollide
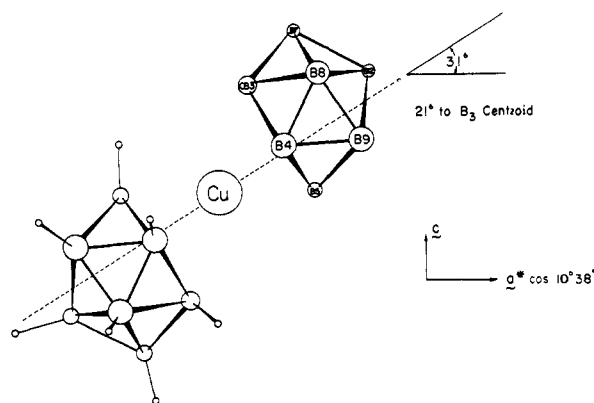

Figure 1. The $Cu(C_2B_9H_{11})_2{}^{2-}$ anion as viewed down its molecular twofold axis (a 10° 38′ counterclockwise rotation about Z). The dotted line represents the perpendicular from copper to the C(2)B(3) carborane face. Hydrogen atoms are pictured on the lower left-hand cage only.

cages in the plane described by B(5), B(7), and B(12). The extent of the distortion (Cu off the cage pseudo-five-fold axis by 0.6 A) can be seen most clearly by reference to Figure 2. Note that the opposite C(2)B(3) faces are required crystallographically to be parallel.

The plane described by Cu in addition to B(5), B(7), and B(12) represents within experimental error a mirror plane. Thus the molecular symmetry is C_{2h} (2/m). Table VI gives analytical results for this plane as well as the best plane representing the open carborane face CB(2), CB(3), B(4), B(5), and B(6).

Table III. Observed and Calculated Structure Amplitudes (×86) (in electrons) for(Et₄N)₂Cu(C₂B₉H₁₁)₂

Table IV. Bond Lengths in $(Et_4N)_2Cu(C_2B_9H_{11})_2{}^a$

Cu–CB(2)	2.584 (7)	B(7)–B(8)	1.78
Cu–CB(3)	2.571 (6)	B(7)–B(11)	1.78
Cu–B(4)	2.214 (8)	B(7)–B(12)	1.79
Cu–B(5)	2.134 (7)	B(8)–B(9)	1.80
Cu–B(6)	2.246 (7)	B(8)–B(12)	1.80
		B(9)–B(10)	1.75
CB(2)–CB(3)	1.53	B(9)–B(12)	1.77
CB(2)–B(6)	1.71	B(10)–B(11)	1.78
CB(2)–B(7)	1.74	B(10)–B(12)	1.80
CB(2)–B(11)	1.71	B(11)–B(12)	1.77
CB(3)–B(4)	1.67		
CB(3)–B(7)	1.76	⟨B–B⟩	1.79
CB(3)–B(8)	1.71		
		⟨Cage–H⟩	1.1 ± 0.1
⟨B–C⟩	1.72		
		N–C(1)	1.56
B(4)–B(5)	1.83	N–C(2)	1.55
B(4)–B(8)	1.80	N–C(3)	1.57
B(4)–B(9)	1.83	N–C(4)	1.50
B(5)–B(6)	1.79	C(1)–C(5)	1.55
B(5)–B(9)	1.78	C(2)–C(6)	1.50
B(5)–B(10)	1.77	C(3)–C(7)	1.56
B(6)–B(10)	1.82	C(4)–C(8)	1.57
B(6)–B(11)	1.82		

^{a} Estimated standard deviation between light atoms is 0.01 A.

Table V. Bond Angles in the $Cu(C_2B_9H_{11})_2{}^{2-}$ Anion^a

Angle	Degrees	Angle	Degrees
CB(2)–Cu–CB(3)	34.6	B(10)–B(11)–B(12)	61.1
CB(3)–Cu–B(4)	39.9	B(12)–B(11)–B(7)	60.5
B(4)–Cu–B(5)	49.9	B(7)–B(11)–CB(2)	59.7
B(5)–Cu–B(6)	48.2	CB(2)–B(11)–B(6)	57.7
B(6)–Cu–CB(2)	40.6	B(10)–B(12)–B(9)	58.4
		B(9)–B(12)–B(8)	60.4
B(6)–B(5)–B(10)	61.8	B(8)–B(12)–B(7)	59.4
B(10)–B(5)–B(9)	58.8	B(7)–B(12)–B(11)	60.3
B(9)–B(5)–B(4)	60.7	B(11)–B(12)–B(10)	59.8
CB(2)–B(6)–B(11)	57.9	B(9)–B(8)–B(4)	61.0
B(11)–B(6)–B(10)	58.3	B(4)–B(8)–CB(3)	56.6
B(10)–B(6)–B(5)	58.5		
B(11)–B(10)–B(12)	59.0	CB(3)–B(8)–B(7)	60.6
B(12)–B(10)–B(9)	59.9	B(7)–B(8)–B(12)	60.0
B(9)–B(10)–B(5)	60.9	B(12)–B(8)–B(9)	59.1
B(5)–B(10)–B(6)	59.6	B(11)–B(7)–B(12)	59.3
B(6)–B(10)–B(11)	60.4	B(12)–B(7)–B(8)	60.6
B(8)–B(9)–B(4)	59.7	B(8)–B(7)–CB(3)	57.7
B(4)–B(9)–B(5)	61.1	CB(3)–B(7)–CB(2)	52.0
B(5)–B(9)–B(10)	60.3	CB(2)–B(7)–B(11)	58.0
B(10)–B(9)–B(12)	61.7	B(4)–CB(3)–B(8)	64.7
B(12)–B(9)–B(8)	60.6	B(8)–CB(3)–B(7)	61.7
CB(3)–B(4)–B(8)	58.7	B(7)–CB(3)–CB(2)	63.4
B(8)–B(4)–B(9)	59.2	CB(3)–CB(2)–B(7)	64.6
B(9)–B(4)–B(5)	58.2	B(7)–CB(2)–B(11)	62.3
B(6)–B(11)–B(10)	61.2	B(11)–CB(2)–B(6)	64.3

Bond Angles in the Tetraethylammonium Ion			
C(1)–N–C(2)	105.9	C(3)–N–C(4)	109.9
C(1)–N–C(3)	107.7	N–C(1)–C(5)	114.0
C(1)–N–C(4)	112.6	N–C(2)–C(6)	114.7
C(2)–N–C(3)	111.6	N–C(3)–C(7)	113.6
C(2)–N–C(4)	109.2	N–C(4)–C(8)	118.0

^{a} Standard deviations in angles is 0.5°.

Generally the features of the dicarbollyl moiety are the same as those found by Zalkin,[8,9] et al.; however, there are several characteristics which distinguish this structure and probably are explicable on the basis of the large distortion described above.

The C–C bond at 1.53 A is significantly shorter than previously found for π-sandwich carborane derivatives (1.61 A in $[C_2B_9H_{11}Re(CO)_3]^-$[9] and 1.58 A
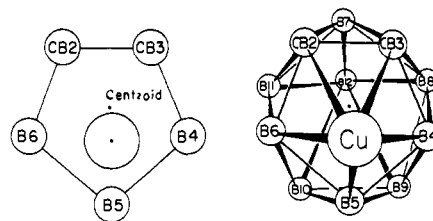

Figure 2. Projection of the $Cu(C_2B_9H_{11})_2{}^{2-}$ anion down the perpendicular to the C(2)B(3) face. Only the far cage is shown.

in $C_2B_9H_{11}FeC_5H_5{}^8$) and reflects the "apparently" small contribution carbon makes in forming the cage to copper bonds. The average Cu–B distance is 2.20 A compared to Cu–C of 2.57 A. This is readily understandable if the cage carbon π electrons "nonbonding" with respect to copper are used in strengthening the carbon to carbon bond.

Table VI. Some Best Least-Squares Planes in the $Cu(C_2B_9H_{11})_2{}^{2-}$ Ion; Orthogonal Coordinates^a

⟵——Plane 1——⟶		⟵——Plane 2——⟶	
Atom	Distance from plane, A	Atom	Distance from plane, A
Cu	0.002	CB(2)	0.027
B(5)	−0.011	CB(3)	0.014
B(7)	0.011	B(4)	−0.046
B(12)	−0.013	B(5)	0.056
CB(2)	−0.78	B(6)	−0.057
CB(3)	0.75	Cu	−1.793
B(4)	1.38		
B(6)	1.40		
B(8)	1.43		
B(9)	0.88		
B(10)	−0.87		
B(11)	−1.41		

^{a} Plane 1: $0.18856X + 0.98184Y + 0.02099Z = 0.00225$; Plane 2: $0.85412X - 0.16244Y + 0.49397Z = -1.79313$.

For the various pentagonal five-atom groupings of cage atoms (e.g., B(7), B(8), B(9), B(10), B(11)), deviations from planarity increase with fractional population by coordinated face atoms. These deviations are commensurate with strong boron to copper bonding and a resulting strengthening of carbon to cage binding.

The observed optical dichroism confirms the presence of the molecular twofold axis alluded to above. In addition the directions of the principal g values, as derived from single-crystal esr measurements,[19] indicate the choice of the Cu to B(4), B(5), B(6) centroid direction as another principal molecular axis.

There are 12 contacts of ca. 3.9 A between the cation and anion, all others being greater than 4 A. These distances are commensurate with the sizes of the groups involved, and thus there seems to be no distortion due to packing.

Summary and Conclusions

Although a complete description of the bonding in the compound will require additional calculations, a

(19) D. D. Scott and A. H. Maki, private communication.

I   II
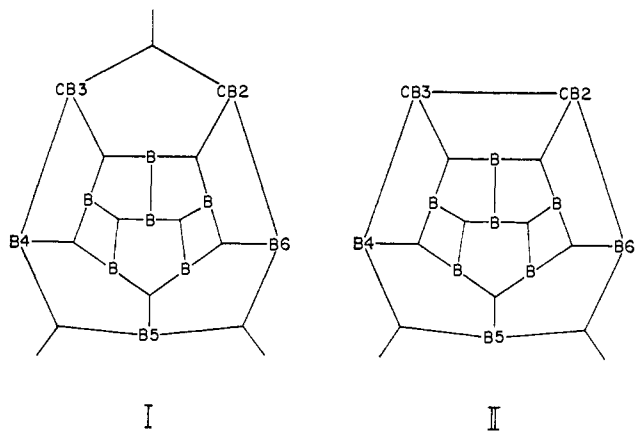
very satisfying topological description is suggested by the short carbon–carbon distance and the close association of the copper with the three cage-face boron atoms.

The usual "symmetrical" interaction of the dicarbollyl ion with a metal ion can be described as in structure I (one of 25 forms), in which three three-center bonds are formed to the metal. Note that the external three-center bonds go to the metal. However, if the cage–metal interaction is limited to the three borons, one could only write two three-center bonds to the metal. This limiting form of interaction (structure II, one of five forms) would have as a feature a localized carbon–carbon bond, and the B(4)–B(5)–B(6) array would be analogous to an anionic, four-electron donor allylic ligand. Thus this distortion, although extreme, is quite similar to that proposed for certain cyclopentadienides.[20] Finally on this basis the copper can be described as a square-planar d^9 system.

(20) M. J. Bennett, M. R. Churchill, M. Gerloch, and R. Mason, *Nature*, **201**, 1318 (1964).