Notes

Structural Characterization of Representative d^7, d^8, and d^9 Transition Metal Complexes of Bis(*o*-carborane)

David E. Harwell, Jeffrey McMillan, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Received May 23, 1997

Introduction

In 1970, Owen and Hawthorne[1−3] reported the synthesis and characterization of a representative series of late transition metal complexes of the chelating ligand bis(*o*-carborane). These anions were 4-coordinate complexes of Cu, Ni, and Co which differ only in their d-electron count (d^7 through d^9, inclusive). While the d^6 Co(III) derivative of the same composition is formally in this series of complexes, an X-ray diffraction study by Love and Bau[4] established that its structure is essentially square pyramidal with the apex occupied by a bridging H atom derived from a nearby BH vertex. While idealized square planar or tetrahedral structures (Figure 1) were assigned to the d^7 and d^8 complexes (excluding the d^9 Cu(II) derivative) on the basis of magnetic data, the determination of the precise structural configuration by X-ray diffraction methods was not possible at the time. However, due to the fact that these complexes containing transition metal−carbon σ bonds displayed extraordinary thermal, oxidative, and hydrolytic stabilities, we have carried out the structural studies described here which revealed bond length and geometric relationships. Consequently, we confirm the structural assignments previously reported for $[M^{4-n}\{(C_2B_{10}H_{10})_2\}_2]^{n-}$ where M = Co(II) (**1**), Ni(II) (**2**), and Cu(III) (**3**) and in addition report the structure of $[Cu\{(C_2B_{10}H_{10})_2\}_2]^{2-}$ (**4**).

Results and Discussion

Synthesis of 1−4. Detailed methods for the preparation of the salts of anions **1**−**4** have been previously described.[1−3] Anions **1**, **2**, and **4** were formed from the reaction of a metal halide ($CoBr_2$, $NiBr_2$, and $CuCl_2$, respectively) with 2 molar equiv of the dilithium salt of bis(*o*-carborane) (Scheme 1). Oxidation of **4** to yield the Cu(III) complex (**3**) was accomplished by the addition of $CuCl_2$.

X-ray Structural Analysis of 1. The coordination of the cobalt atom to the carbon atoms of bis(*o*-carborane) is seen in the skeletal Figure 2. The angle formed by normals to the planes of the two bidentate ligands (defined: C1A, Co1, C1A′ and C1C, Co1, C1C′) is 89°. Therefore, the geometry of the carbon/cobalt framework is best described as tetrahedral. A complete view of the anion (with the exception of hydrogen atoms) can be seen in Figure 3, and selected bond parameters are presented in Table 1. A 2-fold axis passes through **1** (about *x*, $y = {}^1/_4$, $z = {}^1/_4$), and therefore there are two symmetry-related angles of 117.8° (C1A−Co−C1C and C1A′−Co−C1C′), two of 119.0° (C1A−Co−C1C′ and C1A′−Co−C1C), and angles of 92.8° (C1A−Co−C1A′ and C1C−Co−C1C′) about the cobalt atom. Dihedral angles about the carbon−carbon bond within the ligands are both 24(2)°, again due to reasons of symmetry. Distances from the central cobalt atom to the corresponding carbon atoms of the ligands range from 2.051 to 2.070 Å.

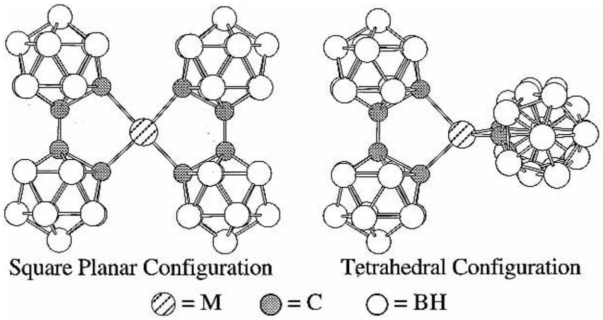

Figure 1. Idealized structural configurations for $[M^{4-n}\{(C_2B_{10}H_{10})_2\}_2]^{n-}$.

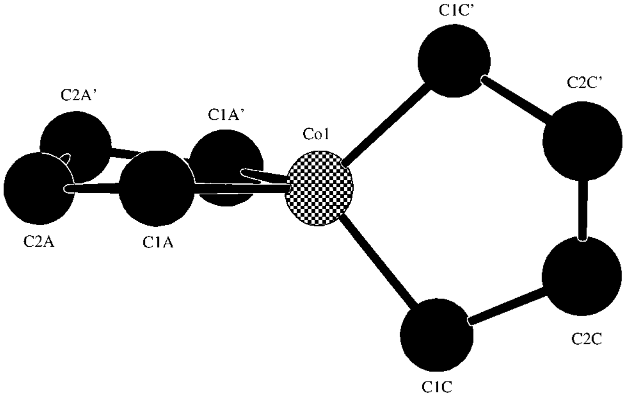

Figure 2. Skeletal view of the cobalt/carbon framework in anion **1** from the crystal structure.

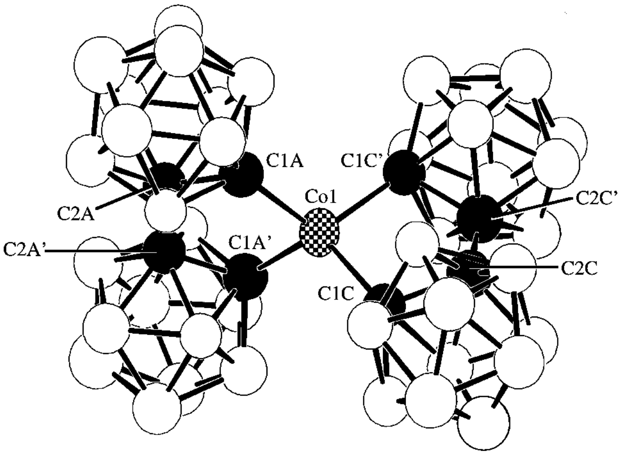

Figure 3. ORTEP representation of anion **1**. Hydrogen atoms are omitted for clarity.

One of the tetraethylammonium cations for **1** is located on a center of symmetry (N on $x = 0$, $y = 0$, $z = 0$), and the other is on a 2-fold axis (about *z*, N1C at $x = {}^1/_4$, $y = 1.2$). Heptane occupies a channel in the crystal and is badly disordered.

X-ray Structural Analysis of 2. Anion **2** is nearly square

---

(1) Owen, D. A. Ph.D. Thesis, University of California, Los Angeles, 1970.

(2) Owen, D. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 3194−3195.

(3) Owen, D. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 873−880.

(4) Love, R. A.; Bau, R. *J. Am. Chem. Soc.* **1972**, *94*, 8274−8276.

S0020-1669(97)00631-9 CCC: $14.00

Scheme 1

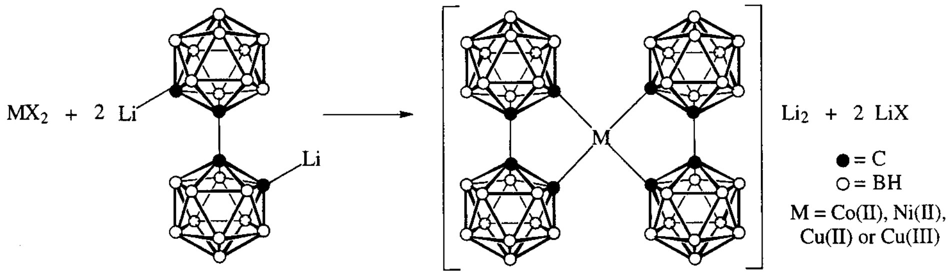

Table 1. Selected Bond Parameters for **1**[a]

Distances (Å)			
Co1−C1A	2.070(12)	Co1−C1C	2.051(11)
C1A−C2A	1.703(15)	C2A−C2A′	1.544(14)
Angles (deg)			
C1A−Co1−C1A′	92.8(4)	C1A−Co1−C1C′	119.0(4)
C1C−Co1−C1C′	92.8(4)	C1A′−Co1−C1C	119.0(4)
C1A−Co1−C1C	117.8(4)	C1A′−Co1−C1C′	117.8(4)
C1A′−C2A′−C2A−C1A	24(2)		
C1C−C2C−C2C′−C1C′	24(2)		
plane (C1A, Co1, C1A′) vs plane (C1C, Co1, C1C′)	89		

[a] atoms designated with primes denote symmetrically equivalent positions at *x*, $^1/_2 - y$, $^1/_2 - z$.

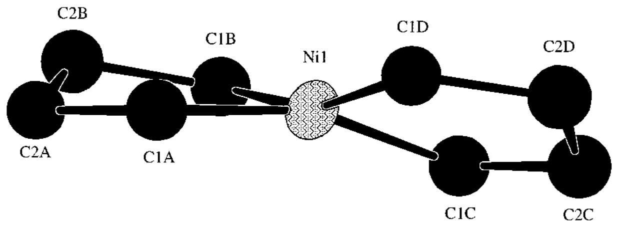

Figure 4. Skeletal view of the nickel/carbon framework in anion **2** from the crystal structure.

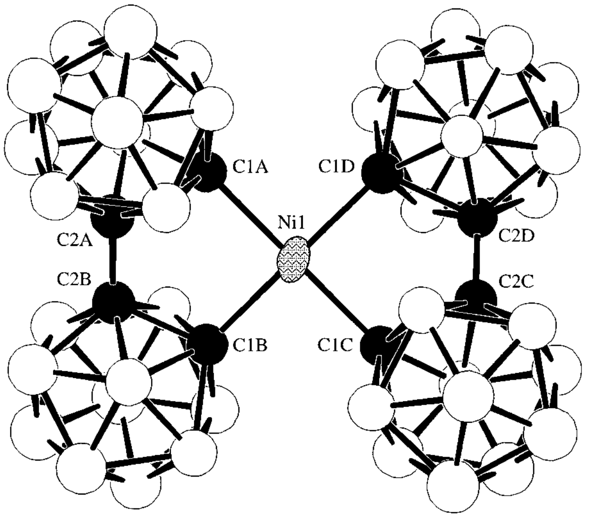

Figure 5. ORTEP representation of anion **2**. Hydrogen atoms are omitted for clarity.

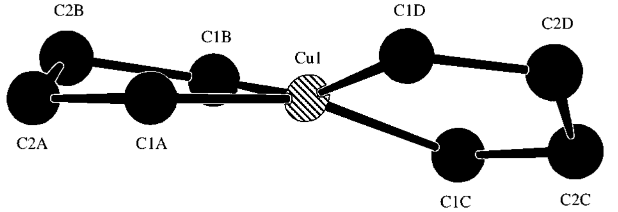

Figure 6. Skeletal view of the copper/carbon framework in anion **3** from the crystal structure.

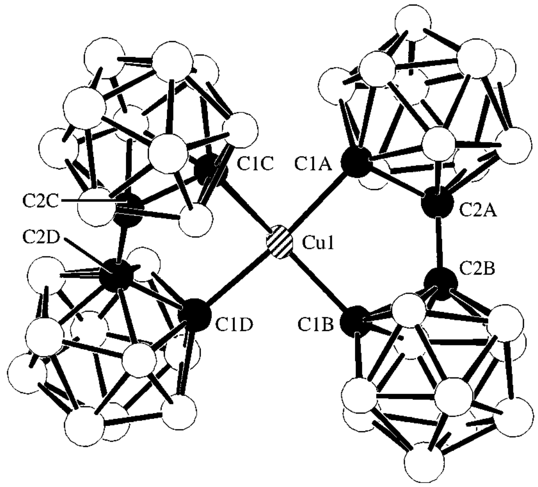

Figure 7. ORTEP representation of anion **3**. Hydrogen atoms are omitted for clarity.

planar, as would be expected for a tetracoordinate d^8 transition metal complex. Figure 4 depicts the nickel/carbon framework of anion **2**, while Figure 5 shows a complete structure of the anion (with the exception of hydrogen atoms). The angle formed by normals to the planes of the two bidentate bis(*o*-carborane) ligands (defined: C1A, Ni1, C1B and C1C, Ni1, C1D) is 26°. This deviation from planarity is most likely due to steric constraints imposed by the two carboranyl ligands. Selected bond parameters for anion **2** are presented in Table 2. *Cis*-bond angles about nickel range from 90.5(4)° (C1A−Ni1−C1B) to 92.4(4)° (C1A−Ni1−C1D), while *trans*-bond angles are 161.6(4)° (C1B−Ni1−C1D) and 162.1(4)° (C1A−Ni1−C1C). The torsion angles within the two bis(*o*-carborane) ligands about the carbon−carbon bond are 28(1)° (C1A−C2A−C2B−C1B) and 19(1)° (C1C−C2C−C2D−C1D). The length of the bonds from the central nickel atom to the attached carbon atoms of the ligands ranges from 1.998(9) to 2.013(9) Å (Ni1−C1C and Ni1−C1D, respectively).

X-ray Structural Analysis of 3. The molecular structure of anion **3** closely resembles that of the anion **2**, as would be expected since both are tetracoordinate d^8 complexes. Figure 6 presents the copper/carbon framework of anion **3**, while Figure 7 depicts the complete structure (with the exception of hydrogen atoms). The angle formed by normals to the planes of the two bidentate bis(*o*-carborane) ligands (defined: C1A, Cu1, C1B and C1C, Cu1, C1D) is 26°, exactly as in anion **2**. This deviation is again justified on the basis of the steric constraints of the carboranyl ligands. Selected bond parameters for anion **3** are presented in Table 3. *Cis*-bond angles about copper range from 90.5(2)° (C1A−Cu1−C1B) to 92.5(2)° (C1A−Cu1−C1C), while *trans*-bond angles are 161.1(2)° (C1B−Cu1−C1D) and 162.4(2)° (C1A−Cu1−C1D). The torsion angles within the two bis(*o*-carborane) ligands about the carbon−carbon bond are 24.0(6)° (C1A−C2A−C2B−C1B) and 23.8(6)° (C1C−

Table 2. Selected Bond Parameters for **2**

Distances (Å)			
Ni1−C1A	2.002(9)	Ni1−C1B	2.002(9)
Ni1−C1C	1.998(9)	Ni1−C1D	2.013(9)
C1A−C2A	1.690(13)	C2A−C2B	1.512(13)
Angles (deg)			
C1A−Ni1−C1B	90.5(4)	C1A−Ni1−C1D	92.4(4)
C1C−Ni1−C1D	91.1(4)	CIB−Ni1−C1C	91.6(4)
C1A−Ni1−C1C	162.1(4)	C1B−Ni1−C1D	161.6(4)
C1A−C2A−C2B−C1B	28(1)		
C1C−C2C−C2D−C1D	19(1)		
plane (C1A, Ni1, C1B) vs plane (C1C, Ni1, C1D)	26		

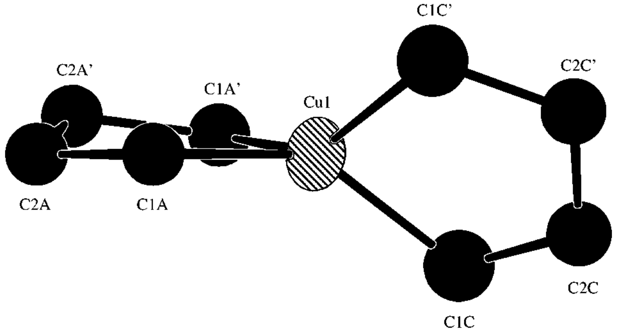

Figure 8. Skeletal view of the copper/carbon framework in anion **4** from the crystal structure.

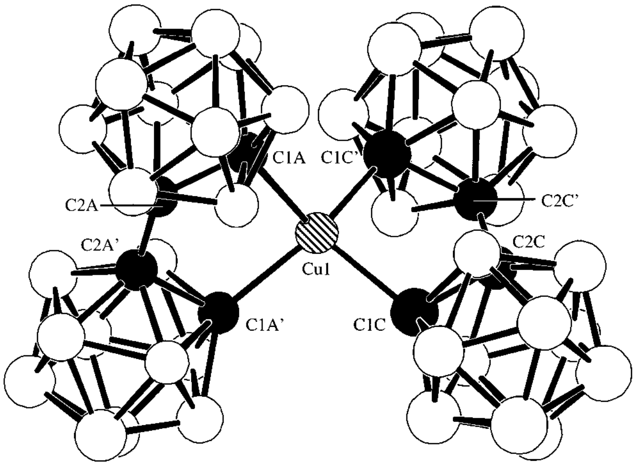

Figure 9. ORTEP representation of anion **4**. Hydrogen atoms are omitted for clarity.

C2C−C2D−C1D). The length of the bonds from the central copper atom to the attached carbon atoms of the ligands ranges from 2.005(6) to 2.031(6) Å (Cu1−C1B and Cu1−C1C, respectively).

X-ray Structural Analysis of 4. It is obvious that the copper/carbon framework of anion **4** is far from planar (Figure 8); however, it is not a simple matter to assign the molecular geometry of the anion either as square planar or as tetrahedral. The angle formed by normals to the planes of the two bidentate ligands (defined: C1A, Cu1, C1A′ and C1C, Cu1, C1C′) is 54°, which is not much closer to 90° (Td) than to 0° (SP). Therefore, the geometry of the carbon/cobalt framework cannot be assigned as either square planar or tetrahedral. A complete view of anion **4** (with the exception of hydrogen atoms) can be seen in Figure 9, and selected bond parameters are presented in Table 4. A 2-fold axis passes through **4** (about $x = {}^1/_2$, $z = {}^1/_4$), and therefore there are two angles of 142.4° (C1A−Cu1−C1C, and C1A′−Cu1−C1C′), two of 102.3° (C1A−Cu1−C1C′ and C1A′−Cu1−C1C) which are related by symmetry, and one each of 90.0 and 89.4° (C1A−Cu1−C1A′ and C1C−Cu1−C1C′, respectively) which are not. Dihedral angles about the carbon−carbon bond within the ligands are 22.3(16)° (C1A−C2A−C2A′−C1A′) and 26.1(17) (C1C−C2C−C2C′−C1C′). Distances from the central copper atom to the corresponding carbon atoms of the ligands range only from 2.070(9) to 2.072(10) Å (Cu1−C1A and Cu1−C1C, respectively).

Table 3. Selected Bond Parameters for **3**

Distances (Å)			
Cu1−C1A	2.029(5)	Cu1−C1B	2.005(6)
Cu1−C1C	2.031(6)	Cu1−C1D	2.015(6)
C1A−C2A	1.669(8)	C2A−C2B	1.517(8)
Angles (deg)			
C1A−Cu1−C1B	90.5(2)	C1A−Cu1−C1D	162.4(2)
C1C−Cu1−C1D	90.5(2)	C1B−Cu1−C1C	92.3(2)
C1A−Cu1−C1C	92.5(2)	C1B−Cu1−C1D	161.1(2)
C1A−C2A−C2B−C1B	24.0(6)		
C1C−C2C−C2D−C1D	23.8(6)		
plane (C1A, Cu1, C1B) vs plane (C1C, Cu1, C1D)	26		

Table 4. Selected Bond Parameters for **4**[a]

Distances (Å)			
Cu1−C1A	2.070(9)	Cu1−C1C	2.072(10)
C1A−C2A	1.661(12)	C2A−C2A′	1.539(12)
Angles (deg)			
C1A−Cu1−C1A′	90.0(3)	C1A−Cu1−C1C′	102.3(4)
C1C−Cu1−C1C′	89.4(4)	C1A′−Cu1−C1C	102.3(4)
C1A−Cu1−C1C	142.4(4)	C1A′−Cu1−C1C′	142.4(4)
C1A−C2A−CA2′−C1A′	22.3(16)		
C1C−C2C−C2C′−C1C′	26.1(17)		
plane (C1A, Cu1, C1A′) vs plane (C1C, Cu1, C1C′)	54		

[a] Atoms designated with primesdenote symmetrically equivalent positions.

Conclusions

As suggested by magnetic susceptibility measurements,[2,3] the structural configuration of anion **1** is tetrahedral and the configurations of anions **2** and **3** are distorted square planar. The configuration of anion **4** is intermediate between square planar and tetrahedral, thus explaining the ambiguity encountered in previous attempts to assign its geometry on the basis of only magnetic measurements. This intermediate structure might be expected for a 4-coordinate d^9 transition metal complex which did not benefit significantly from either configuration.

Anion **1** displays very little deviation from its idealized tetrahedral geometry (Figure 2). However, due to constraints imposed by the bis(*o*-carborane) ligands, anions **2** and **3** adopt a twisted bowtie conformation which deviates slightly from the idealized square planar geometry expected for a tetracoordinate d^8 transition metal compound (Figures 4 and 6, respectively).

As mentioned above, the crystal structure of $[Et_4N][Co\{(C_2B_{10}H_{10})_2\}_2]$ was previously reported by Bau.[4] This electron-deficient complex was found to contain a Co−H−B interaction derived from the central cobalt atom and a terminal hydrogen atom associated with one of the adjacent B−H vertices of the bis(*o*-carborane) ligand. This Co−H−B bridge expands the coordination sphere of cobalt from 4- to 5-coordinate, and the complex is seen to adopt a geometry which resembles square pyramidal.

Experimental Section

General Considerations. Many attempts have been made during the past 20 years to prepare suitable crystals of anions **1**−**4**. Over 30 solvent combinations were tried, and 6 different counterions used. We

Table 5. Details of Crystallographic Data Collection for **1**−**4**[f]

	1	**2**	**3**	**4**
formula	$C_{24}H_{80}B_{40}CoN_2$[a]	$C_{40}H_{112}B_{40}N_2Ni$	$C_{16}H_{60}B_{40}CuN$	$C_{40}H_{112}B_{40}CuN_2$
fw	888.3[a]	1112.9	763.0	1117.7
temp (°C)	25	25	25	25
wavelength (Å)	1.5418	0.7107	1.5418	0.7107
space group	*Pnna*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
a (Å)	19.247(3)	11.859(3)	13.3000(9)	19.249(2)
b (Å)	20.153(2)	14.119(5)	13.5657(8)	16.144(1)
c (Å)	17.191(2)	21.331(6)	14.820(1)	23.611(2)
α (deg)		82.921(9)	114.130(2)	
β (deg)		76.988(8)	108.756(2)	105.932(3)
γ (deg)		85.428(8)	99.917(2)	
V ($Å^3$)	6668	3448	2163	7056
Z	4	2	2	4
calcd density (g cm^{-3})	*e*	1.01	1.17	1.05
μ (cm^{-1})	*e*	3.1	7.8	3.4
R^b	0.094	0.081	0.066	0.098
$R_w{}^c$	0.096	0.087	0.095	0.111
GOF[d]	1.81	2.23	2.77	3.05

[a] Calculation does not include solvent. [b] $R = \sum||F_o| - |F_c||/|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$. [d] GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. [e] Because this crystal contains an uncertain amount of disordered solvent, the density and absorption coefficient cannot be calculated. [f] Collection parameters for the Rigaku AFC5 diffractometer: $A = 0.945$, $B = 0.3$, fractional offset (M) $= 0.5$, scan width $= (A + B \tan \theta)$ with 50% of the scan width on each side of the center.

report only the ones that worked. Details of crystallographic data collection for the salts of anions **1**−**4** are presented in Table 5. Atoms were located by use of heavy atom methods. Data were collected at 25 °C in the $\theta-2\theta$ scan mode. Data were corrected for Lorentz and polarization effects and for secondary extinction, but only compounds **1** and **4** were corrected for absorption. All calculations were performed on a VAX3100 computer in the J. D. McCullough X-ray Crystallography Laboratory. Scattering factors for hydrogen were obtained from ref 5, and those for other atoms, from ref 6.

Programs used in this work include locally modified versions of the following: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; ABSCOR, absorption correction based on *ψ* scans; SHELX76 (Sheldrick), a crystal structure package; SHELX86 (Sheldrick), a crystal structure solution package; ORTEP (Johnson). These programs are all included in the UCLA crystallographic package.

Collection and Reduction of X-ray Data for the Tetraethylammonium Salt of 1. A purple crystal, obtained from a CH_2Cl_2/heptane solution, was placed in a capillary with solvent and mounted on a Rigaku AFC5R diffractometer. Systematic absences were found for 0*k*1 reflections for which $k + l = 2n + 1$, for *h*01 reflections for which $h + \mathrm{l} = 2n + 1$, and for *hk*0 reflections for which $h = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 13 accurately centered reflections ($16.1 < 2\theta < 27.8°$). Three intense reflections ($1\bar{4}1$, $\bar{1}03$, $2\bar{1}3$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (53.15 h). Of the 3720 unique reflections measured, 1287 were considered observed ($I > 2\sigma(I)$) and were used in the subsequent structure analysis.

Solution and Refinement of the Structure of the Tetraethylammonium Salt of 1. Co and four cation C atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. All methyl and methylene H atoms were included in calculated positions; C−H = 1.0 Å, H−C−H = 109.5°. Carboranyl H atoms were located and were included, but parameters were not refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Anomalous dispersion terms were included for the scattering of Co. The largest peak on a final difference electron density map was 0.2 e $Å^{-3}$.

Collection and Reduction of X-ray Data for the Tetrabutyammonium Salt of 2. An orange crystal, obtained from a CH_2Cl_2/pentane solution, was mounted on a fiber and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 29 accurately centered reflections ($8.6 < 2\theta < 18.4°$). Three intense reflections ($03\bar{1}$, 115, $2\bar{3}\bar{2}$) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (111.8 h). Of the 6344 unique reflections measured, 3196 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent analysis.

Solution and Refinement of the Structure of the Tetrabutylammonium Salt of 2. Ni and cation N and C atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. Methylene and methyl carbon atoms were included in calculated positions; C−H = 1.0 Å. Hydrogens on the carborane ligand were included in located positions. H atoms were assigned the isotropic displacement values based approximately on the value for the attached atom. Anomalous dispersion terms were included for Ni. The largest peak on a final difference electron density map was 0.2 e $Å^{-3}$. C2E has been included at two locations, at 0.8 and 0.2 occupancies for C2E and C2E′, respectively.

Collection and Reduction of X-ray Data for the Tetraethylammonium Salt of 3. A yellow crystal, obtained from an Et_2O solution, was mounted on a fiber and placed on a Syntex $P\bar{1}$ diffractometer modified by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 22 accurately centered reflections ($19.1 < 2\theta < 40.5°$). Three intense reflections ($2\bar{4}\bar{1}$, $3\bar{1}2$, $11\bar{4}$) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 3% during the course of the experiment (33.7 h). Of the 5925 unique reflections measured, 4647 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent analysis.

Solution and Refinement of the Structure of the Tetraethylammonium Salt of 3. All anion non-hydrogen atoms were refined with anisotropic parameters. All cation non-hydrogen atoms were refined with isotropic parameters. All cation hydrogens were included in calculated positions as members of rigid groups; C−H = 1.0 Å, H−C−H = 109.5°. Hydrogens on the carborane ligand were included in located positions. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Anomalous dispersion terms were included for the scattering of Cu. The largest peak on a final difference electron density map was 0.3 e $Å^{-3}$.

Collection and Reduction of X-ray Data for the Tetrabutylammonium Salt of 4. A purple crystal, obtained from a CH_2Cl_2/pentane solution, was placed on a fiber mounted on the Huber diffractometer. Systematic absences were found for *hk*0 reflections for which $h + k = 2n + 1$ and *h*0*l* reflections for which $l = 2n + 1$. Unit cell parameters were determined from a least-squares fit of 47 accurately centered

---

(5) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(6) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

reflections ($7.7 < 2\theta < 19.2°$). Three intense reflections ($3\bar{3}\bar{1}$, $33\bar{2}$, 024) were monitored every 97 reflections to check stability. Intensities of these reflections decayed 9% during the course of the experiment (97.5 h). Of the 9318 unique reflections measured, 2317 were considered observed ($I > 3\sigma(I)$) and were used in the subsequent structure analysis.

Solution and Refinement of the Structure of the Tetrabutylammonium Salt of 4. Cu and all C atoms were refined with anisotropic parameters. All other non-hydrogen atoms were refined with isotropic parameters. Methyl carbon atoms of two of the *n*-butyl groups were refined at half-occupancy in two positions. No solvent is present in the crystal. Methyl and methylene H atoms were included in calculated positions; C−H = 1.0 Å, H−C−H = 109.5°. Carboranyl H atoms were located and were included, but parameters were not refined. H atoms were assigned isotropic displacement values based approximately on the value for the attached atom. Anomalous dispersion terms were included for the scattering of Cu. The largest peak on a final difference electron density map, near Cu, was 0.44 e $Å^{-3}$.

Acknowledgment. This work was funded by the National Science Foundation under Grant CHE-93-14037.

Supporting Information Available: Atom-numbered ORTEP projections and tables giving crystallographic data collection details, positional parameters, and thermal parameters for **1**−**4** (16 pages). Ordering information is given on any current masthead page.

IC9706313