mers of penicillamine are indicative of the optically active surface of BSA near the sulfhydryl group.

The present results indicate that once the ligand reaches the protein surface, removal of metal ions can occur very rapidly. The rate at which metal ions are removed from the body is undoubtedly limited more by rates of biological transport than by chemical kinetics.

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Synthesis and Properties of Cobalt Complexes Containing the Bidentate π-Bonding $B_8C_2H_{10}^{4-}$ Ligand

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In two recent communications[1,2] we have briefly described the preparation of two cobalt complexes which were structurally characterized by crystallographic studies[2,3] and shown to contain a unique bidentate π-bonding ligand, $B_8C_2H_{10}^{4-}$ (Figure 1). The subject cobalt complexes (I and II) contained formal Co^{3+} ions π-bonded to each open five-membered face of the $B_8C_2H_{10}^{4-}$ ion as shown in Figures 2 and 3. We have, as described earlier, coined the trivial name (3,6)-1,2-dicarbacanastide(4−) to describe the $B_8C_2H_{10}^{4-}$ ion.[4]

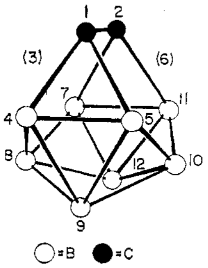

Figure 1.—Schematic drawing of the (2,6)-dicarbacanastide ion with H atoms omitted.

Results and Discussion

Complexes I and II illustrated in Figures 2 and 3 were formed in the same reaction mixture in 15 and 6% yields, respectively. The reaction sequence which leads to the formation of I and II is, in essence, the base degradation of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co^{III}]^-$, III, with aqueous hydroxide ion in the presence of added Co^{2+} ion. Both I and II could be obtained by employing preformed III or by generating III *in situ* from the (3)-1,2-$B_9C_2H_{12}^-$ ion with aqueous hydroxide ion in the presence of Co^{2+} ion. The latter method of preparing certain bis(π-dicarbollyl)(transition metal) complexes has been previously described.[5] The preliminary reactions presumably involved are illustrated below and lead to the unobserved $(B_9C_2H_{11})Co(B_8C_2H_{10})^{3-}$ intermediate (IV).

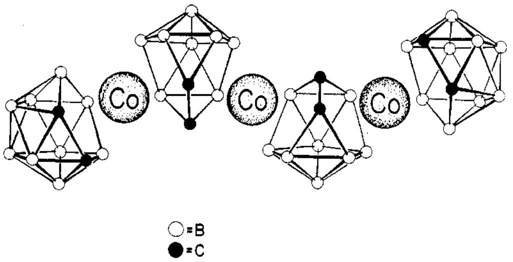

Figure 3.—Schematic drawing of $[(B_9C_2H_{11})Co(B_8C_2H_{10})]_2Co^{3-}$ ion (II) with H atoms omitted.

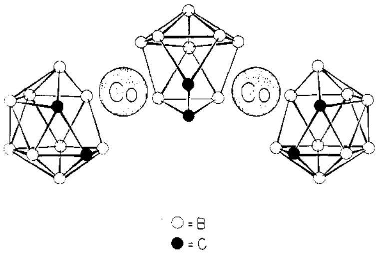

Figure 2.—Schematic drawing of $(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})^{2-}$ ion (I) with H atoms omitted.

$$B_9C_2H_{12}^- + OH^- \rightleftharpoons B_9C_2H_{11}^{2-} + H_2O$$

$$4B_9C_2H_{11}^{2-} + 3Co(OH)_2 \longrightarrow \underset{\text{III}}{2(B_9C_2H_{11})_2Co^-} + 6OH^- + Co$$

$$\underset{\text{III}}{(B_9C_2H_{11})_2Co^-} + 2OH^- + H_2O \longrightarrow \underset{\text{IV}}{(B_9C_2H_{11})Co(B_8C_2H_{10})^{3-}} + H_2 + B(OH)_3$$

Following the formation of IV, attack by Co^{2+} and an extraneous $B_9C_2H_{11}^{2-}$ ion (formed *in situ via* degradation of III) leads to I. If, however, IV reacts with a Co^{2+} ion followed by reaction with 1 additional equivalent of IV, the resulting product is II.[6]

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(1) J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).

(2) M. R. Churchill, A. H. Reis, J. N. Francis, and M. F. Hawthorne, *ibid.*, **92**, 4993 (1970).

(3) A. Zalkin, D. J. St. Clair, and D. H. Templeton, *Abstr. Amer. Crystallogr. Ass.*, 58 (1968).

(4) We have in the past generated trivial names for carborane ligands from Spanish nouns which describe the geometry of the ligand. Since the known $B_8C_2H_{10}^{4-}$ ion resembles a basket, we have named the ion (3,6)-1,2-dicarbacanastide(4−) based upon the Spanish noun "canasta" (basket). As in the case of the dicarbollide ions, we have placed the carbon atoms in their lowest possible numerical state and indicated the two boron atoms which were removed from the icosahedron to generate the open π-bonding faces by placing them in parentheses. The icosahedron is numbered conventionally.

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

(6) The intermediate IV, when generated in the absence of added Co^{2+} ion, apparently rearranges and accepts a proton from solvent to form a $(B_9C_2H_{11})Co(B_8C_2H_{11})^{2-}$ ion which contains formal Co^{3+}. In addition, ionic products having molecular weights considerably greater than those of I and II appear to be formed in the presence of Co^{2+} after long reaction time. Details of these two aspects of dicarbacanastide ion chemistry will be presented elsewhere.

The infrared spectra of I and II were grossly similar in the fingerprint region and no obvious absorbances characteristic of the dicarbacanastide ligand could be found. The characteristic absorbances of the tetramethylammonium salts of I and II are listed in the Experimental Section.

The 32.1-MHz nmr spectra of I and II consisted of meaningless broad resonances which appeared between −20 and +20 ppm [relative to $BF_3 \cdot O(C_2H_5)_2$]. The proton nmr spectrum of I consisted of a singlet at δ 4.28, area 2, assigned to CH protons of the $B_8C_2H_{10}{}^{4-}$ ligand and a singlet at δ 3.29, area 4, assigned to CH protons of the $B_9C_2H_{11}{}^{2-}$ ligand. Similarly, the proton nmr spectrum of II consisted of a singlet at δ 4.13, area 4, assigned to CH protons of the $B_8C_2H_{10}{}^{4-}$ ligand and a singlet at δ 3.12, area 4, assigned to the CH protons of the $B_9C_2H_{11}{}^{2-}$ ligand.

The electronic spectra of I and II were characterized by intense absorption maxima at higher frequencies. Table I presents these data and the corresponding spectroscopic properties of III.

TABLE I

ELECTRONIC SPECTRA OF I–III IN CH_3CN, λ_{max}, mμ (ϵ)

I	II	III
210 (7000)	209 (26,000)	205 (35,000)
292 (30,000)	290 (44,000)	290 (58,000)
454 sh (410)	324 (31,000)	350 sh (38,000)
		430 sh (11,000)

Cyclic voltammetry of I–III illustrated reversible one-electron oxidation and reduction couples which are shown in Table II.

TABLE II

CYCLIC VOLTAMMETRY REDOX COUPLES, $E_{1/2}$ *vs.* SCE[a]

Process	I	II	III
Ion + e^-	−1.46	−1.36	−1.53
Ion − e^-	+1.57	+1.07	+0.70

[a] Acetonitrile solution, 0.1 *N* in $(C_2H_5)_4NClO_4$ supporting electrolyte; reversible half-peak reduction potentials reported.

While it is impossible at this time to interpret the electronic spectral data, the absence of more complicated cyclic voltammetry results in the cases of I and II points to the addition and removal of single electrons from the lowest unfilled and highest filled molecular orbitals, respectively. If I and II did not contain extended molecular orbital arrays, one might expect to see discrete redox reactions at each of the multiple formal Co^{3+} ions present in these species. Thus, we feel that each cobalt atom is well aware of the presence of its partner(s) in I and II.

Experimental Part

All chemicals used were of reagent grade; J. T. Baker 3405 silica gel was used for the chromatographic separations, poured into the column as a slurry with the solvent used. Infrared spectra were obtained on a Perkin-Elmer Model 421 sodium chloride spectrophotometer as Nujol mulls. Analyses were conducted by Schwarzkopf Analytical Laboratories. The ^{11}B nmr spectra were obtained on a Varian HA-100 spectrometer at 32 MHz; positions are reported in ppm from boron trifluoride etherate. Pmr spectra were obtained on a Varian A-60 spectrometer.

Compounds I and II could be prepared starting from either $1,2\text{-}B_9C_2H_{12}{}^-(CH_3)_3NH^+$ or $(1,2\text{-}B_9C_2H_{11})_2Co^-K^+$; the difference in procedure concerns only the preparation of the initial reaction mixture. The results in each case were identical.

From $(1,2\text{-}B_9C_2H_{11})_2Co^-K^+$.—To a solution of 66 g of NaOH in 90 ml of water in a 250-ml erlenmeyer flask was added 2.8 g (7.75 mmol) of $(1,2\text{-}B_9C_2H_{11})_2Co^-K^+$ and a solution of 5 g (20 mmol) of $CoCl_2 \cdot 6H_2O$ in 10 ml of water.

From $1,2\text{-}B_9C_2H_{12}{}^-(CH_3)_3NH^+$.—To a 100-ml round-bottomed flask containing 3 g (15.5 mmol) of $1,2\text{-}B_9C_2H_{12}{}^-(CH_3)_3NH^+$ was added 25 ml of a hot solution prepared by dissolving 66 g of NaOH in 90 ml of water. The flask was placed on a rotary evaporator with a steam bath for 5 min to remove the trimethylamine. The solution was then poured into a 250-ml erlenmeyer flask containing 6 g (25 mmol) of $CoCl_2 \cdot 6H_2O$ in 10 ml of water, and the remainder of the still hot NaOH solution was added.

The open flask was placed on a steam bath for 2 hr. The liquid temperature should be about 90°. At the end of this time, equal volumes of ice and of water were added to the reaction mixture to cool and dilute it, and the whole was filtered to remove cobalt hydroxide and metal. The filtrate was extracted with three 75-ml portions of ether, and the combined extracts were washed with 50 ml of half-saturated NaCl solution. The ether was dried over several successive portions of $CaCl_2$, which caused a dark red-brown oil to separate, coating the drying agent. New portions of $CaCl_2$ were used until no more oil separated after standing for 30 min. The ether [containing unreacted $(1,2\text{-}B_9C_2H_{11})_2Co^-$] was decanted, and the oil and $CaCl_2$ were taken up in water. A rotary evaporator was used to remove residual ether from this solution, which contained most of the desired products. The large anions were precipitated with excess $(CH_3)_4N^+$ ion, and the collected, dried product was taken up in 3:2 CH_2Cl_2–CH_3CN, using about 20 ml of solvent for each gram of material. This solution was chromatographed with this solvent in 1–5-ml portions on a 2-cm diameter column of 100 ml (dry measure) of silica gel. With flow rates no greater than 1 drop/sec two red-brown bands developed; the first was I; the second, II.

Each band was collected, reduced to dryness on the rotary evaporator, and taken up in acetone–water. One or two drops of 50% aqueous $(CH_3)_4N^+Cl^-$ was added, and the solutions were boiled down until crystallization started. Cooling, filtering, washing with small amounts of cold water, and drying afforded 0.7 g of I, 15%, and 0.3 g of II, 6%. Both compounds tended to trap solvent molecules within the crystal, although under these conditions only II did so, with two molecules of acetone per formula weight. Recrystallization from ethanol–water gave a brown solid with no solvent in the crystal.

I, $(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})[N(CH_3)_4]_2$.—*Anal.* Calcd for $C_{14}H_{56}B_{26}Co_2N_2$: C, 25.81; H, 8.66; B, 43.14; N, 4.30. Found: C, 25.94; H, 8.48; B, 41.53; N, 4.51. Infrared spectrum, cm^{-1} (intensity): 2488 (s), 1267 (w), 1221 (w), 1192 (w), 1136 (m), 1090 (m), 1055 (w), 1018 (m), 991 (w), 975 (sh), 964 (s), 937 (s), 901 (w), 868 (m), 752 (w), 715 (m), and 681 (w).

II, $[(B_9C_2H_{11})Co(B_8C_2H_{10})]_2Co[N(CH_3)_4]_3$.—*Anal.* Calcd for $C_{20}H_{78}B_{34}Co_3N_3$: C, 30.57; H, 8.88; B, 35.99; N, 4.11. Found: C, 30.79; H, 10.24; B, 34.67; N, 4.05. Infrared spectrum of monohydrate, cm^{-1} (intensity): 3600 (w), 2463 (s), 1598 (w), 1278 (w), 1242 (w), 1132 (m), 1092 (m), 1000 (m), 977 (sh), 961 (m), 949 (m), 906 (sh), 864 (m), 749 (m), 718 (m), and 679 (w).

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