The metal–nitrogen stretching region provided no distinctive information with regard to geometric identity. Cyclic voltammetry indicates that the pyridine and acetonitrile complexes undergo reversible oxidation to the ruthenium(III) state and that both isomers exhibit essentially the same redox potential (Table V).

Acknowledgment. The support of a Cottrell College Science Grant, of the National Science Foundation for purchase of the spectrophotometer, and of Air Products Corp. for analyses is gratefully acknowledged. We also thank the National Science Foundation for support through NSF-EPSCOR Grant ISP 8011447, the State of Arkansas, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $Ru(phen)_2CO_3$, 71603-93-5; *cis*-$[Ru(phen)_2(py)_2](PF_6)_2$, 85370-13-4; *trans*-$[Ru(phen)_2(py)_2](PF_6)_2$, 85549-97-9; *cis*-$[Ru(phen)_2(CH_3CN)_2](PF_6)_2$, 85370-15-6; *trans*-$[Ru(phen)_2(CH_3CN)_2](PF_6)_2$, 85439-56-1; *trans*-$[Ru(phen)_2(OH_2)_2](PF_6)_2$, 85439-54-9; *cis*-$[Ru(phen)_2(OH)_2](PF_6)_2$, 85370-16-7; *trans*-$[Ru(phen)_2(CH_3CN)(H_2O)](PF_6)_2$, 85370-18-9.

Supplementary Material Available: Listings of positional parameters for hydrogen atoms, anisotropic thermal parameters, and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Structural Characterization of $3'{:}2\text{-}[2',4'\text{-}C_2B_5H_6][1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6]$: A Coupled-Cage Cobaltacarborane Containing a Boron–Boron Linkage

ROBERT P. MICCICHE, JEFFREY S. PLOTKIN, and LARRY G. SNEDDON*[1]

Received September 8, 1982

The molecular structure of $3'{:}2\text{-}[2',4'\text{-}C_2B_5H_6][1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6]$ has been determined from the single-crystal X-ray diffraction data. In agreement with the structure previously proposed on the basis of the spectroscopic data, the compound was shown to be a two-cage complex consisting of a $1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ cobaltacarborane unit linked to a $2',4'\text{-}C_2B_5H_6$ carborane cage by means of a two-center boron–boron single bond. The cage geometry of the $1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ is based on a tricapped trigonal prism, while that of the $2',4'\text{-}C_2B_5H_6$ unit is based on a pentagonal bipyramid. Crystal data: space group $P\bar{1}$, $Z = 2$, $a = 9.155$ (3) Å, $b = 15.659$ (11) Å, $c = 7.142$ (2) Å, $\alpha = 99.64$ (4)°, $\beta = 101.11$ (3)°, $\gamma = 100.69$ (5)°, $V = 965$ (2) Å^3. The structure was refined by full-matrix least-squares methods to a final R of 0.047 and R_w of 0.047 for the 2085 reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The number and variety of multicage boron compounds have increased significantly in the last few years because of the development of new synthetic procedures for the formation of cage linkages. The availability of these compounds has now allowed initial investigations of the chemistry and properties of these unique species that have already demonstrated that these compounds will be an important area of future research. We, in particular, have become interested in the formation and properties of multimetal, multicage boron clusters and have already reported[2] that the reaction of $(\eta\text{-}C_5H_5)Co(CO)_2$ with an isomeric mixture of the coupled-cage carborane $(2,4\text{-}C_2B_5H_6)_2$ results in the formation of six isomeric cobaltacarboranes. Each of these complexes was proposed on the basis of spectroscopic data to be composed of a $(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ cobaltacarborane linked by means of a boron–boron single bond to a $2,4\text{-}C_2B_5H_6$ carborane cage. We also demonstrated that at elevated temperatures these coupled cage complexes underwent three different types of reversible rearrangements until at 400 °C an equilibrium mixture of 12 different isomeric compounds was produced. We report here the structural characterization of one of these compounds.[3]

Experimental Section

Several crystals of the compound were grown over a 12-h period by evaporation of a dilute heptane solution. A very thin rectangular-shaped crystal, 0.484 × 0.125 × 0.030 mm, was selected for data collection, mounted on a glass fiber, and then transferred to the diffractometer. The Enraf-Nonius program SEARCH was used to obtain 25 reflections, which were then used in the program INDEX to obtain an orientation matrix for data collection. This orientation matrix was improved by the substitution of new reflections, and refined cell dimensions and their standard deviations were obtained from the least-squares refinement of these 25 accurately centered reflections. Crystal data: $Co_2C_{14}B_{10}H_{22}$, mol wt 416.31, space group $P\bar{1}$, $Z = 2$, $a = 9.155$ (3) Å, $b = 15.659$ (11) Å, $c = 7.142$ (2) Å, $\alpha = 99.64$ (4)°, $\beta = 101.11$ (3)°, $\gamma = 100.69$ (5)°, $V = 965$ (2) Å^3, ρ(calcd) = 1.433 g cm^{-3}. The mosaicity of the crystal was judged acceptable on the basis of several θ scans.

Collection and Reduction of Data. The diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer interfaced with a PDP 8/A computer, employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. A combined $2\theta,\omega$-scan technique was used to record the intensities of all reflections for which $1.0 < 2\theta < 50°$. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program DATARD. Of the 3395 measured intensities, 2085 had $F_o^2 > 3\sigma(F_o^2)$ and were used in the analysis.

Solution and Refinement of Structure. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure determination package.[4]

Normalized structure factors were calculated by using a K curve, and the intensity distribution statistics support a centrosymmetric space group. A three-dimensional Patterson synthesis gave the coordinates of the cobalt atoms. Full-matrix least-squares refinement of these coordinates, with use of preliminary scale and thermal parameters from the Wilson plot, followed by a subsequent Fourier map phased on these refined coordinates, led to the location of the remaining heavy atoms of the complex. Anisotropic least-squares refinement of these atoms followed by a difference Fourier synthesis resulted in the location

---

[1] Alfred P. Sloan Foundation Fellow.

[2] Plotkin, J. S.; Sneddon, L. G. *Inorg. Chem.* **1979**, *18*, 2165.

[3] Compound II in ref 2.

[4] Enraf-Nonius Inc., Garden City Park, NY.

0020-1669/83/1322-1765$01.50/0 © 1983 American Chemical Society

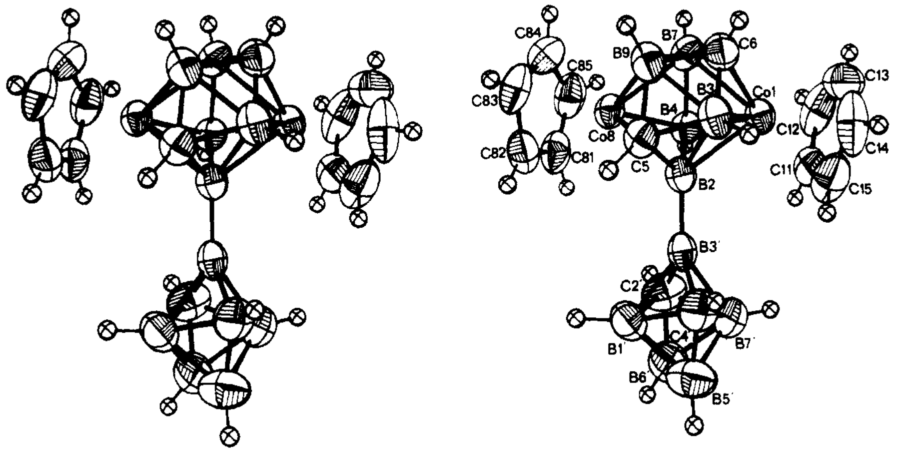

Figure 1. ORTEP stereodrawing of 3′:2-[2′,4′-$C_2B_5H_6$][1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$]. Non-hydrogen atoms are shown as 50% thermal ellipsoids.

Table I. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*
Co1	0.3557 (1)	0.11436 (6)	0.2707 (1)
Co8	0.6849 (1)	0.26357 (6)	0.3903 (1)
C11	0.2114 (9)	0.0760 (5)	0.0050 (10)
C12	0.2687 (8)	0.0072 (5)	0.0447 (10)
C13	0.2313 (10)	−0.0150 (5)	0.2028 (12)
C14	0.1425 (9)	0.0395 (6)	0.2650 (11)
C15	0.1329 (8)	0.0981 (5)	0.1399 (13)
C81	0.7965 (8)	0.3356 (5)	0.2247 (10)
C82	0.8208 (8)	0.3893 (4)	0.4053 (10)
C83	0.8957 (8)	0.3476 (5)	0.5412 (10)
C84	0.9134 (8)	0.2675 (5)	0.4418 (11)
C85	0.8530 (7)	0.2607 (5)	0.2407 (11)
C6	0.4829 (8)	0.1251 (4)	0.5313 (8)
C5	0.5330 (7)	0.2886 (4)	0.5413 (8)
C4′	0.2316 (7)	0.3758 (4)	0.2511 (9)
C2′	0.3686 (8)	0.3589 (5)	0.0172 (9)
B4	0.5261 (8)	0.1781 (5)	0.1882 (9)
B2	0.4429 (8)	0.2576 (5)	0.3184 (10)
B7	0.5938 (8)	0.1282 (5)	0.3905 (10)
B3	0.4007 (9)	0.2052 (5)	0.5436 (11)
B9	0.6097 (10)	0.2171 (5)	0.6214 (10)
B3′	0.3534 (8)	0.3227 (5)	0.2018 (10)
B6′	0.2702 (11)	0.4249 (6)	−0.0506 (14)
B5′	0.1732 (12)	0.4372 (6)	0.1182 (14)
B1′	0.3745 (10)	0.4414 (5)	0.2018 (13)
B7′	0.1840 (10)	0.3265 (6)	0.0168 (13)

Table II. Intramolecular Bond Distances (Å)

1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ Cage			
Co1-B4	1.936 (6)	C6-B9	1.618 (8)
Co1-C6	1.958 (5)	C6-B7	1.561 (8)
Co1-B3	2.129 (6)	B7-B9	1.934 (8)
Co1-B7	2.139 (6)	C11-C12	1.330 (10)
Co1-B2	2.182 (6)	C12-C13	1.322 (11)
Co1-C11	2.016 (6)	C13-C14	1.362 (12)
Co1-C12	2.039 (6)	C14-C15	1.385 (13)
Co1-C13	2.058 (7)	C15-C11	1.346 (10)
Co1-C14	2.071 (8)	C81-C82	1.370 (8)
Co1-C15	2.023 (7)	C82-C83	1.400 (9)
Co1-Co8	3.316 (1)	C83-C84	1.387 (9)
Co8-B4	1.952 (6)	C84-C85	1.415 (9)
Co8-C5	1.972 (5)	C85-C81	1.379 (9)
Co8-B9	2.093 (6)	HB4-B4	1.10 (4)
Co8-B7	2.129 (7)	HB7-B7	1.06 (4)
Co8-B2	2.156 (6)	HB3-B3	1.09 (4)
Co8-C81	2.049 (6)	HB9-B9	1.00 (4)
Co8-C82	2.098 (6)	HC5-C5	1.02 (4)
Co8-C83	2.097 (6)	HC6-C6	0.93 (4)
Co8-C84	2.040 (6)	HC11-C11	0.90 (4)
Co8-C85	2.038 (6)	HC12-C12	0.94 (4)
B2-B3	1.994 (9)	HC13-C13	0.92 (4)
B2-C5	1.592 (7)	HC14-C14	0.76 (4)
B2-B4	1.798 (8)	HC15-C15	0.86 (4)
B2-B3′	1.654 (8)	HC81-C81	0.86 (4)
B3-C6	1.576 (8)	HC82-C82	0.99 (4)
B3-C5	1.613 (8)	HC83-C83	0.84 (4)
B3-B9	1.851 (10)	HC84-C84	0.90 (4)
B4-B7	1.815 (9)	HC85-C85	1.01 (4)
C5-B9	1.557 (8)		
2′,4′-$C_2B_5H_6$ Cage			
C2′-B1′	1.669 (9)	B1′-B6′	1.821 (11)
C2′-B7′	1.671 (9)	B7′-B3′	1.851 (9)
C2′-B3′	1.540 (8)	B7′-B5′	1.793 (11)
C2′-B6′	1.568 (10)	B7′-B6′	1.781 (11)
C4′-B1′	1.641 (9)	B5′-B6′	1.636 (11)
C4′-B7′	1.658 (9)	HB1′-B1′	1.00 (4)
C4′-B3′	1.568 (8)	HB7′-B7′	1.03 (4)
C4′-B5′	1.553 (9)	HC2′-C2′	0.75 (4)
B1′-B3′	1.833 (9)	HC4′-C4′	0.85 (4)
B1′-B5′	1.810 (11)		

of 20 hydrogen atoms. The positions of the remaining two hydrogens, HB5′ and HB6′, were calculated and included (but not refined) in the structure factor calculations. Final refinement with a numerical absorption correction (transmission coefficient: maximum 89.62%, minimum 49.90%), including anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters (3.89) for the hydrogen atoms, yielded the final residual factors $R = 0.047$ and $R_w = 0.047$.

The full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $(4F_o/\sigma(F_o)^2)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[5a] and those for hydrogen[5b] from Stewart. The effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values[6] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The final positional parameters are given in Table I. Intramolecular bond distances and selected bond angles are presented in Tables II and III. Figure 1 shows a stereoscopic view of the complete molecule. Listings of final thermal parameters, selected molecular planes, hydrogen atom positions, and observed and calculated structure factors and a unit cell packing diagram are available as supplementary material.

Results and Discussion

The completed structural determination of the title compound confirms the gross geometry previously proposed[2] on the basis of the spectroscopic data. As can be seen in the ORTEP drawing presented in Figure 1, the compound is composed of a 1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$ cobaltacarborane cluster that is bound to a 2′,4′-$C_2B_5H_6$ carborane cage by

---

(5) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. J. *J. Chem. Phys.* **1965**, *43*, 3175.

(6) Cromer, D. T.; Ibers, J. A. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. Selected Bond Angles (deg)

$1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$ Cage							
B4–Co1–C6	91.5 (2)	B4–B2–B3	103.5 (4)	B7–B4–Co1	69.4 (3)	B9–B7–Co8	61.8 (3)
B4–Co1–B3	94.2 (2)	B4–B2–Co1	57.2 (3)	B2–B4–Co8	70.1 (3)	B9–B7–Co1	96.7 (4)
B4–Co1–B7	52.6 (2)	B4–B2–Co8	58.3 (3)	B2–B4–Co1	71.4 (3)	Co8–B7–Co1	102.0 (3)
B4–Co1–B2	51.4 (2)	B3–B2–Co1	61.1 (2)	Co8–B4–Co1	117.1 (3)	C5–B9–C6	104.0 (5)
C6–Co1–B3	45.1 (2)	B3–B2–Co8	94.9 (3)	B9–C5–B2	113.8 (4)	C5–B9–B3	55.7 (4)
C6–Co1–B7	44.5 (2)	Co1–B2–Co8	99.7 (2)	B9–C5–B3	71.5 (4)	C5–B9–B7	104.0 (4)
C6–Co1–B2	85.2 (2)	B3–B2–B3′	129.8 (4)	B9–C5–Co8	71.7 (3)	C5–B9–Co8	63.4 (3)
B3–Co1–B7	75.7 (3)	Co1–B2–B3′	123.2 (4)	B2–C5–B3	76.9 (4)	C6–B9–B3	53.5 (3)
B3–Co1–B2	55.1 (2)	B4–B2–B3′	120.2 (4)	B2–C5–Co8	73.6 (3)	C6–B9–B7	51.2 (3)
B7–Co1–B2	78.0 (2)	Co8–B2–B3′	127.9 (4)	B3–C5–Co8	116.8 (4)	C6–B9–Co8	108.0 (4)
B4–Co8–C5	90.7 (2)	C5–B2–B3′	122.4 (4)	B3–C6–B9	70.8 (4)	B3–B9–B7	87.6 (4)
B4–Co8–B9	94.3 (3)	C6–B3–C5	103.4 (5)	B3–C6–B7	113.3 (5)	B3–B9–Co8	101.5 (4)
B4–Co8–B7	52.6 (2)	C6–B3–B9	55.7 (4)	B3–C6–Co1	73.2 (3)	B7–B9–Co8	63.7 (3)
B4–Co8–B2	51.6 (2)	C6–B3–B2	103.0 (4)	B9–C6–B7	74.9 (4)	C12–C11–C15	108.1 (8)
C5–Co8–B9	44.9 (2)	C6–B3–Co1	61.7 (3)	B9–C6–Co1	116.6 (4)	C11–C12–C13	110.1 (8)
C5–Co8–B7	84.5 (2)	C5–B3–B9	52.9 (3)	B7–C6–Co1	73.9 (3)	C12–C13–C14	108.0 (9)
C5–Co8–B2	45.1 (2)	C5–B3–B2	51.1 (3)	C6–B7–B4	111.2 (5)	C13–C14–C15	106.5 (8)
B9–Co8–B7	54.5 (2)	C5–B3–Co1	107.4 (4)	C6–B7–B9	53.9 (3)	C11–C15–C14	107.3 (8)
B9–Co8–B2	76.7 (3)	B9–B3–B2	86.6 (4)	C6–B7–Co8	108.7 (4)	C82–C81–C85	110.2 (6)
B7–Co8–B2	78.8 (2)	B9–B3–Co1	99.7 (4)	C6–B7–Co1	61.6 (3)	C81–C82–C83	107.2 (6)
C5–B2–B4	110.7 (4)	B2–B3–Co1	63.8 (2)	B4–B7–B9	104.7 (4)	C82–C83–C84	108.3 (6)
C5–B2–B3	52.0 (3)	B7–B4–B2	97.7 (4)	B4–B7–Co8	58.7 (3)	C83–C84–C85	107.5 (7)
C5–B2–Co1	105.8 (4)	B7–B4–Co8	68.7 (3)	B4–B7–Co1	58.0 (3)	C81–C85–C84	106.7 (6)
C5–B2–Co8	61.3 (3)						
$2',4'\text{-}C_2B_5H_6$ Cage							
B3′–C2′–B6′	120.5 (6)	B2–B3′–B1′	138.6 (4)	C4′–B5′–B6′	101.5 (6)	B3′–B1′–B6′	95.2 (5)
B3′–C2′–B1′	69.5 (4)	B2–B3′–B7′	145.1 (5)	C4′–B5′–B1′	57.8 (4)	B3′–B1′–B5′	96.4 (5)
B3′–C2′–B7′	70.3 (4)	C4′–B3′–C2′	94.6 (5)	C4′–B5′–B7′	58.9 (4)	B6′–B1′–B5′	53.6 (4)
B6′–C2′–B1′	68.4 (5)	C4′–B3′–B1′	57.1 (4)	B6′–B5′–B1′	63.6 (5)	C4′–B7′–C2′	86.6 (5)
B6′–C2′–B7′	66.6 (5)	C4′–B3′–B7′	57.3 (4)	B6′–B5′–B7′	62.4 (5)	C4′–B7′–B3′	52.7 (3)
B1′–C2′–B7′	85.9 (5)	C2′–B3′–B1′	58.6 (4)	B1′–B5′–B7′	78.3 (5)	C4′–B7′–B6′	91.8 (5)
B3′–C4′–B5′	120.9 (5)	C2′–B3′–B7′	58.2 (4)	C4′–B1′–C2′	87.3 (5)	C4′–B7′–B5′	53.3 (4)
B3′–C4′–B1′	69.7 (4)	B1′–B3′–B7′	76.3 (4)	C4′–B1′–B3′	53.3 (3)	C2′–B7′–B3′	51.6 (3)
B3′–C4′–B7′	70.0 (4)	C2′–B6′––B5′	102.5 (6)	C4′–B1′–B6′	90.9 (5)	C2′–B7′–B6′	53.9 (4)
B5′–C4′–B1′	69.0 (5)	C2′–B6′–B1′	58.5 (4)	C4′–B1′–B5′	53.2 (4)	C2′–B7′–B5′	92.2 (5)
B5′–C4′–B7′	67.8 (5)	C2′–B6′–B7′	59.5 (4)	C2′–B1′–B3′	51.9 (4)	B3′–B7′–B6′	95.9 (5)
B1′–C4′–B7′	87.2 (5)	B5′–B6′–B1′	62.9 (5)	C2′–B1′–B6′	53.2 (4)	B3′–B7′–B5′	96.3 (5)
B2–B3′–C4′	132.1 (5)	B5′–B6′–B7′	63.1 (5)	C2′–B1′–B5′	91.7 (5)	B6′–B7′–B5′	54.5 (4)
B2–B3′–C2′	133.1 (5)	B1′–B6′–B7′	78.4 (5)				

means of a boron–boron single bond.

Although a number of boron–boron linked multicage boron clusters have now been synthesized, only six of these compounds have been structurally characterized: $1{:}1'\text{-}[B_5H_8]_2$,[7] $2{:}2'\text{-}[1\text{-}SB_9H_8]_2$,[8] $1{:}5'\text{-}[B_{10}H_{13}]_2$,[9] $2{:}2'\text{-}[B_{10}H_{13}]_2$,[10] $2{:}6'\text{-}[B_{10}H_{13}]_2$,[10] and $2'{:}4\text{-}[B_{10}H_{13}][7\text{-}\{(PMe_2Ph)_2Pt\}B_{10}H_{11}]$.[11] In the present case, the linkage between the two cages is formed by a boron–boron bond between atoms B2–B3′. The B2–B3′ distance of 1.654 (8) Å is significantly shorter than any of the previously determined cage linkages: $1{:}1'\text{-}[B_5H_8]_2$, 1.74 (6) Å; $2{:}2'\text{-}[1\text{-}SB_9H_8]_2$, 1.678 (5) Å; $1{:}5'\text{-}[B_{10}H_{13}]_2$, 1.698 (3) Å; $2{:}2'\text{-}[B_{10}H_{13}]_2$, 1.692 (3) Å; $2{:}6'\text{-}[B_{10}H_{13}]_2$, 1.679 (3) Å; and $2'{:}4\text{-}[B_{10}H_{13}][7\text{-}\{(PMe_2Ph)_2Pt\}B_{10}H_{11}]$, 1.707 (15) Å. It is not clear whether the variations in bond lengths among these clusters are related to steric or electronic factors in these compounds, but in the coupled-cage cobaltacarborane complex there appear to be no significant steric interactions between the $2',4'\text{-}C_2B_5H_6$ carborane cage and either the cobaltacarborane cage or the cyclopentadienyl rings. For example, the closest interactions between the cages are B3′-C5, 2.844 Å, B3′-HC5, 2.943 Å, and B3′-B4, 2.992 Å, while the closest contacts between the $2',4'\text{-}C_2B_5H_6$ cage and the cyclopentadienyl rings are HB7′–HC15, 2.777 Å, and HB7′–HC11, 2.778 Å. The absence of steric restrictions should allow the cages to approach quite closely and may account for the shortened linkage distance.

The cobaltacarborane cage adopts the tricapped-trigonal-prismatic structure, which previously has been confirmed[12] by Grimes for the parent cluster, $1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$, and which is consistent with its $2n + 2$ closo skeletal electron count (9 cage atoms, 20 skeletal electrons). Thus, atoms Co1, B2, and B3 and atoms Co8, B7, and B9 form the triangular faces of the prism, while atoms B1, C2, and C3 occupy four-coordinate positions capping the rectangular faces of the prism. The bond distances and angles in the cage are almost identical with those observed in the parent and are within normal ranges for metallaboron cage systems, with the exception that the B3–B2, 1.994 (9) Å, and B7–B9, 1.934 (8) Å, distances are unusually long. Similar long distances for B3–B2, 1.98 (1) Å, and B7–B9, 1.92 (1) Å, were found in the parent cobaltacarborane, and it was suggested[12] that since each of these boron–boron bonds forms an edge of a four-sided face that is capped by a carbon atom, the long bond lengths may be caused by withdrawal of electron density from the four-sided faces by the coordinated CH groups. The long B2–B3 distance is also interesting in light of our previous observation[2] that the $2',4'\text{-}C_2B_5H_6$ cage bound at B2 can readily migrate to the B3 position at 220 °C to form an equilibrium mixture of $3'{:}3\text{-}[2',4'\text{-}C_2B_5H_6][1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6]$ and $3'{:}2\text{-}[2',4'\text{-}C_2B_5H_6][1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6]$. Cage atom

---

(7) Grimes, R. N.; Wang, F. E.; Lewin, R.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1961**, *47*, 996.

(8) Pretzer, W. R.; Rudolph, R. W. *J. Chem. Soc., Chem. Commun.* **1974**, 629.

(9) Brown, G. M.; Pinson, J. W.; Ingram, L. L., Jr. *Inorg. Chem.* **1979**, *18*, 1951.

(10) Boocock, S. K.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1980**, 790.

(11) Boocock, S. K.; Greenwood, N. N.; Kennedy, J. D.; McDonald, W. S.; Staves, J. *J. Chem. Soc., Dalton Trans.* **1981**, 2573.

(12) Grimes, R. N.; Zalkin, A.; Robinson, W. T. *Inorg. Chem.* **1976**, *15*, 2274.

rearrangements in the cobaltacarborane cage (340°) and the carborane cage (400°) were observed only at much higher temperatures; therefore, we proposed that the 2′,4′-$C_2B_5H_6$ cage migration must occur by means of a direct shift mechanism possibly involving intermediates in which the carborane cage boron B3′ adopts a bridging position across cobaltacarborane cage atoms B2 and B3. We have, in fact, recently reported[13] the first structural characterization of this type of single three-center boron cage linkage in another coupled-cage cobaltacarborane complex, 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$][2′,3′-$(CH_3)_2C_2B_4H_5$], providing additional support for the involvement of such species in these rearrangements. The observation of a lengthened B2–B3 distance is also consistent with a direct shift mechanism of rearrangement since it would indicate a lower bonding interaction between these two atoms, which should facilitate the transfer of the 2′,4′-$C_2B_5H_6$ cage by means of a three-center, B2, B3′, B3, intermediate. It should be noted, however, that the B3′–B3 distance, 3.305 Å, and the HB3–B2′ distance, 2.814 Å, indicate little interaction between these atoms in the solid state at room temperature.

The structure of the 2′,4′-$C_2B_5H_6$ cage is based on a pentagonal bipyramid, with atoms B1 and B7 occupying the apex positions. The cage bond distances and angles are again normal and are consistent with those determined in a microwave study[14] of the parent carborane, 2,4-$C_2B_5H_7$, apparently indicating that there has been little perturbation of the cage bonding caused by the attachment of the cobaltacarborane fragment at the B3′ position.

Further studies are now in progress concerning the synthesis and structural characterizations of related linked cage clusters, and these will be reported in future publications.

Acknowledgment. We thank the Army Research Office, the National Science Foundation, and the University of Pennsylvania Materials Research Laboratory for support of this research.

Registry No. 3′:2-[2′,4′-$C_2B_5H_6$][1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_6$], 70480-08-9.

Supplementary Material Available: Tables of selected molecular planes, hydrogen atom positional parameters, anisotropic thermal parameters, and observed and calculated structure factors and an ORTEP molecular packing diagram (19 pages). Ordering information is given on any current masthead page.

---

(13) Borelli, A. J., Jr.; Plotkin, J. S.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 1328.

(14) Beaudet, R. A.; Poynter, R. L. *J. Chem. Phys.* **1965**, *43*, 2166.

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Structure Proofs of Ligated and Polymeric Dioxomolybdenum(VI)–Tridentate Complexes: $MoO_2(C_5H_3N\text{-}2,6\text{-}(CH_2S)_2)(C_4H_8SO)$ and $[MoO_2(C_5H_3N\text{-}2,6\text{-}(CH_2O)_2)]_n$

JEREMY M. BERG[1] and R. H. HOLM*

Received September 10, 1982

The dioxomolybdenum(VI) complexes $MoO_2(L\text{-}NS_2)\cdot$TMSO and $[MoO_2(L\text{-}NO_2)]_n$ (where L-NS_2 = pyridine-2,6-dimethanethiolate, L-NO_2 = pyridine-2,6-dimethanolate, and TMSO = tetramethylene sulfoxide) have been prepared and structurally characterized by single-crystal X-ray diffraction methods. Crystals of the former compound consist of isolated mononuclear units, each having a distorted octahedral environment around Mo with cis-oxo groups and trans-thiolate donors. The remaining coordination sites are occupied by the N atom of the pyridine and an O-bound sulfoxide. Crystals of the latter consist of polymeric chains of Mo complexes, each of which has a distorted octahedral environment similar to that in the former complex with alkoxide replacing thiolate and an oxo group, unsymmetrically bridging from an adjacent complex, replacing the sulfoxide oxygen. Both compounds crystallize in the space group $P2_1/c$ with a = 8.508 (4) Å, b = 10.784 (7) Å, c = 16.961 (4) Å, and β = 110.08 (4)° for $MoO_2(L\text{-}NS_2)\cdot$TMSO and a = 7.490 (2) Å, b = 14.335 (4) Å, c = 8.310 (2) Å, and β = 113.72 (2)° for $[MoO_2(L\text{-}NO_2)]_n$. The final agreement factors are R = 2.85%, R_w = 2.91% and R = 2.50%, R_w = 2.55%, respectively. These compounds provide the first structurally characterized examples of MoO_2(tridentate) systems, which may be important as models of the catalytic sites of certain molybdenum-containing enzymes.

The known molybdenum-containing enzymes,[2] with the exception of nitrogenase, catalyze transformations that may be described as oxygen atom transfer reactions (e.g., $NO_3^- \rightarrow NO_2^-$, $SO_3^{2-} \rightarrow SO_4^{2-}$). Evidence from EPR[2-4] and EXAFS[5,6] studies indicates that the oxidized enzymes contain Mo(VI), which is coordinated by one or more terminal (t) oxo and at least two sulfur ligands. Those Mo–S distances of ~2.4 Å deduced from EXAFS analysis involve thiolate ligands. We are engaged in research directed toward the attainment of credible synthetic representations of the catalytic sites of certain molybdoenzymes in oxidized and reduced forms. A potentially useful feature of such species is the presence of a labile coordination site for substrate binding and activation. This feature is presumably present in complexes of the type MoO_2(tridentate)·D, examples of which have been described[7-10] (D = neutral monodentate ligand). Additionally,

---

(1) National Science Foundation Predoctoral Fellow, 1980–1983.

(2) Bray, R. C. *Enzymes, 3rd ed.* **1975**, *12*, Chapter 6.

(3) Gutteridge, S.; Bray, R. C. In "Molybdenum and Molybdenum-Containing Enzymes"; Coughlan, M., Ed.; Pergamon Press: New York, 1980; pp 221–239.

(4) Lamy, M. T.; Gutteridge, S.; Bray, R. C. *Biochem. J.* **1980**, *185*, 397.

(5) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721.

(6) Bordas, J.; Bray, R. C.; Garner, C. D.; Gutteridge, S.; Hasnain, S. S. *Biochem. J.* **1980**, *199*, 499.

(7) Liebeskind, L. S.; Sharpless, K. B.; Wilson, R. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 7061.

(8) Rajan, O. A.; Chakravorty, A. *Inorg. Chim. Acta* **1979**, *37*, L503; *Inorg. Chem.* **1981**, *20*, 660.

(9) Topich, J. *Inorg. Chim. Acta* **1980**, *46*, L37; *Inorg. Chem.* **1981**, *20*, 3704.

(10) Dey, K.; Maiti, R. K.; Bhar, J. K. *Transition Met. Chem. (N.Y.)* **1981**, *6*, 345.

0020-1669/83/1322-1768$01.50/0