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Crystal and Molecular Structures of Two Thermally Interconvertible Metallocarborane Isomers, 1,8,5,6- and 1,7,5,6- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$. Reversible Metal–Metal Bond Formation in a Polyhedral Surface

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The structures of the title compounds were established from single-crystal x-ray diffraction investigations and found to consist of nine-vertex tricapped trigonal prisms with the cobalt atoms occupying adjacent vertices in the 1,7,5,6 isomer and nonadjacent vertices in the 1,8,5,6 isomer, in agreement with the structures originally proposed from NMR studies. Both compounds crystallize in the monoclinic space group $C2/c$. For the 1,8,5,6 isomer, $a = 24.138$ (6) Å, $b = 7.803$ (2) Å, $c = 16.127$ (4) Å, $\beta = 111.26$ (4)°, and $d_{\text{meas}} = 1.54$ g cm⁻³ ($d_{\text{calcd}} = 1.56$ g cm⁻³ for $Z = 8$). For the 1,7,5,6 isomer, $a = 15.959$ (2) Å, $b = 7.846$ (2) Å, $c = 23.049$ (3) Å, $\beta = 102.33$ (2)°, and $d_{\text{calcd}} = 1.56$ g cm⁻³ for $Z = 8$. The structures were refined by full-matrix least-squares procedures to final R values 0.053 and 0.054 for the 1,8,5,6 and 1,7,5,6 compounds, respectively. The observed Co–Co bond distance of 2.444 (2) Å and the calculated value of 2.07 Å for the nearest H–H intramolecular contact between C_5H_5 rings in the 1,7,5,6 isomer offer some support for the hypothesis that the thermal equilibrium between the two isomers at elevated temperature reflects opposing tendencies toward metal–metal bond formation and steric repulsion of the C_5H_5 rings in the 1,7,5,6 system.

Introduction

A recent investigation of thermal rearrangements in small polyhedral metallocarboranes by Miller and Grimes³ disclosed a previously unreported phenomenon in boron cage chemistry—*reversible* thermal migration of metal atoms on the polyhedral surface. Of the two such systems examined, the seven-vertex 1,7,2,3- and 1,2,4,5- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_3\text{H}_5$ isomers and the nine-vertex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$ species, the latter example was the better defined, and equilibrium constant measurements were conducted at several temperatures. The two isomers involved, red 1,8,5,6- and green 1,7,5,6- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$, had previously been prepared from reactions of the carborane 2,4- $\text{C}_2\text{B}_5\text{H}_7$ with cobalt reagents in solution⁴ or in the vapor phase.⁵ From ¹¹B and ¹H NMR evidence, the structures of the two isomers were proposed³ to be tricapped trigonal prisms, with the cobalt atoms occupying nonadjacent (1,8) locations in the 1,8,5,6 isomer and adjacent (1,7) vertices in the 1,7,5,6 isomer; in both species the cage carbon atoms were judged to be in capping (5,6) positions on the polyhedron.

The two compounds were found to undergo reversible thermal interconversion in the vapor phase at elevated temperatures,³ with $K_{\text{eq}} = [1,7,5,6]/[1,8,5,6] = 1.00 \pm 0.05$ at 340 °C and an extrapolated value of 6 ± 1 at 25 °C. From measurements of K_{eq} at several temperatures, the value of ΔH for the 1,8,5,6 \rightarrow 1,7,5,6 rearrangement was calculated to be -2 ± 1 kcal. Aside from the desirability of establishing precise molecular parameters and confirming the proposed geometries of these molecules, three additional considerations prompted us to initiate crystal structure determinations: (1) comparison of the Co–Co distance in the 1,7,5,6 isomer with other metallocarborane metal–metal bonds; (2) testing of the previous suggestion³ that the driving force for separation of the $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$ groups at elevated temperatures is due to steric crowding of the cyclopentadienyl rings in the 1,7,5,6 isomer; (3) the fact that no dimetallic cobaltacarboranes of less than ten cage atoms, with the exception of the triple-decked sandwich species 1,7,2,3-⁶ and 1,7,2,4- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{-(CH}_3)_2\text{C}_2\text{B}_3\text{H}_4$,⁷ had been crystallographically characterized.

Experimental Section

Samples of 1,8,5,6- and 1,7,5,6- $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_5\text{H}_7$ (isomers A and B, respectively), obtained from the "direct-insertion" reaction of 2,4- $\text{C}_2\text{B}_5\text{H}_7$ with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}(\text{CO})_2$ in the vapor phase,⁵ were recrystallized⁸ from pentane to give dark red A and dark green B. The crystal of A selected for precession photography and data collection

Table I. Crystallographic Data^a

	Isomer	
	1,8,5,6	1,7,5,6
Space group	$C2/c$	$C2/c$
a , Å	24.138 (6)	15.959 (2)
b , Å	7.803 (2)	7.846 (2)
c , Å	16.127 (4)	23.049 (3)
β , deg	111.26 (4)	102.33 (2)
Z	8	8
R	0.053	0.054
R_w	0.071	0.064
No. of crystal faces	8	6
Max crystal dimension, mm	0.40	0.33
Min crystal dimension, mm	0.22	0.10
Crystal vol, mm ³	0.038	0.0062
d_{meas} , g cm ⁻³	1.54 ^b	c
d_{calcd} , g cm ⁻³	1.56	1.56

^a Distances are given in angstroms and angles in degrees, and estimated standard deviations in the least significant digits are shown in parentheses. ^b Measured by flotation in aqueous KI. ^c Not measured.

was an irregularly shaped thick plate, and that of B was a well-formed rhombohedron. The maximum and minimum crystal dimensions and volumes are given in Table I. For both crystals, precession photography employing Cu $K\alpha$ radiation indicated the conditions limiting possible reflections to be hkl ($h + k = 2n$), $h0l$ ($l = 2n$), and $0k0$ ($k = 2n$). The possible space groups are thus $C2/c$ and Cc . Since the centric space group $C2/c$ subsequently was found to provide a satisfactory model in each case, the noncentric group Cc was not further tested.

Alignment and data collection were conducted for each compound on a Hilger and Watts four-circle, computer-controlled diffractometer using Mo $K\alpha$ (λ 0.7107 Å) radiation at 23 °C. Unit cell constants, determined in each instance from a least-squares refinement of the setting angles for 12 reflections, are given in Table I together with other relevant data. The numbers given in parentheses in Table I and throughout the paper are estimated standard deviations in the least significant figure quoted and were derived from the inverse matrix in the course of normal least-squares refinement calculations. The intensity data were collected with a θ - 2θ step-scan over a range of $1 \leq \theta \leq 24.0^\circ$ for isomer A and $1 \leq \theta \leq 23.0^\circ$ for isomer B. Stationary-counter 21- and 18-s background counts were taken for A and B, respectively, at the limits of each scan. For isomer A, a symmetric scan range of 0.84° in θ , centered on the calculated peak position, was composed of 84 steps of 1-s duration each; in the case of isomer B, a scan range of 0.72° in θ composed of 72 steps of 1 s each was employed. In both cases, reflections with a count range exceeding 8000/s were brought within the linear response range of

Table II. Final Positional and Thermal Parameters for 1,8,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C01	0.1262 (0)	0.0899 (1)	0.0053 (1)	0.0023 (0)	0.0152 (2)	0.0057 (1)	-0.0011 (1)	0.0016 (0)	-0.0020 (1)
C08	0.1181 (0)	0.3722 (1)	0.1544 (1)	0.0016 (0)	0.0131 (2)	0.0042 (0)	0.0000 (0)	0.0009 (0)	0.0003 (1)
B2	0.1428 (5)	0.357 (1)	0.0386 (7)	0.0040 (3)	0.016 (2)	0.0060 (5)	-0.0033 (6)	0.0023 (3)	-0.0031 (7)
B3	0.2080 (5)	0.191 (1)	0.0915 (7)	0.0023 (2)	0.024 (2)	0.0078 (6)	-0.0003 (6)	0.0019 (3)	-0.0022 (9)
B4	0.0784 (4)	0.246 (1)	0.0472 (6)	0.0019 (2)	0.021 (2)	0.0050 (4)	0.0003 (5)	0.0012 (2)	-0.0006 (7)
C5	0.1941 (4)	0.362 (1)	0.1331 (7)	0.0027 (2)	0.030 (2)	0.0097 (6)	-0.0023 (6)	0.0028 (3)	-0.005 (1)
C6	0.1810 (5)	0.055 (1)	0.1325 (6)	0.0033 (3)	0.027 (2)	0.0071 (5)	0.0012 (6)	0.0009 (3)	0.0002 (8)
B7	0.1167 (5)	0.104 (1)	0.1328 (7)	0.0034 (3)	0.014 (2)	0.0069 (5)	0.0003 (5)	0.0023 (3)	-0.0001 (7)
B9	0.1918 (5)	0.214 (2)	0.1932 (7)	0.0024 (3)	0.031 (3)	0.0069 (6)	0.0043 (7)	0.0005 (3)	-0.002 (1)
C11	0.3613 (8)	0.445 (2)	0.1118 (9)	0.0058 (5)	0.040 (3)	0.0085 (7)	-0.006 (1)	0.0047 (6)	-0.008 (1)
C12	0.1568 (7)	0.090 (2)	0.4368 (8)	0.0053 (5)	0.034 (3)	0.0077 (7)	-0.003 (1)	0.0027 (5)	0.003 (1)
C13	0.108 (1)	0.150 (1)	0.4527 (8)	0.0112 (9)	0.016 (2)	0.0086 (7)	0.005 (1)	0.0059 (8)	0.0022 (9)
C14	0.0602 (7)	0.043 (3)	0.412 (1)	0.0043 (4)	0.067 (6)	0.013 (1)	0.010 (1)	0.0045 (6)	0.024 (2)
C15	0.4204 (8)	0.408 (2)	0.1286 (8)	0.0052 (5)	0.045 (4)	0.0066 (6)	0.001 (1)	0.0007 (5)	-0.007 (1)
C81	0.1297 (5)	0.464 (1)	0.2804 (5)	0.0036 (3)	0.026 (2)	0.0040 (4)	0.0022 (7)	0.0014 (3)	-0.0023 (7)
C82	0.3676 (4)	0.097 (1)	0.2716 (6)	0.0030 (2)	0.021 (2)	0.0062 (5)	0.0013 (5)	0.0018 (3)	0.0043 (7)
C83	0.4222 (5)	0.109 (1)	0.3451 (6)	0.0037 (3)	0.017 (2)	0.0070 (5)	-0.0015 (5)	0.0025 (3)	0.0014 (7)
C84	0.0422 (4)	0.471 (1)	0.1657 (6)	0.0022 (2)	0.024 (2)	0.0087 (6)	0.0008 (5)	0.0024 (3)	-0.0034 (9)
C85	0.0744 (5)	0.386 (1)	0.2419 (7)	0.0045 (3)	0.020 (2)	0.0076 (5)	0.0017 (7)	0.0039 (4)	0.0018 (8)

^a The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

the scintillation counter by means of calibrated attenuators. The intensities of three standard reflections for each compound were monitored at regular intervals during data collection and exhibited no significant trends. Data were corrected for Lorentz and polarization (*Lp*) factors and then for absorption ($\mu(\text{Mo K}\alpha) = 24.03$ for A and 24.17 for B) using Gaussian integration.⁹ The maximum and minimum absorption corrections were 2.681 and 1.565 for A and 1.570 and 1.254 for B. After averaging of the intensities of equivalent reflections as well as those recorded more than once, the data were reduced to 2222 and 1968 independent reflections, of which 1648 and 848 had $F^2 \geq 3\sigma(F^2)$ for A and B, respectively, where $\sigma(F^2)$ was estimated from counter statistics as described elsewhere.¹⁰ Only these latter reflections were utilized in the final refinements of structure factors.

Solution and Refinement of the Structure

Standard three-dimensional Patterson syntheses for A and B contained several strong peaks which were assigned to Co-Co vectors in each isomer. Full-matrix least-squares refinement based on *F* for the cobalt atoms alone gave conventional *R* values of 0.355 and 0.237 Å for A and B, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The function minimized¹¹ was $\sum w(|F_o| - |F_c|)^2$, and the weights *w* were taken as $4F_o^2 / \sigma(F_o^2)^2$ where $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber¹² and those for hydrogen from Stewart.¹³ Difference Fourier syntheses based on these cobalt atom positions in each case revealed all remaining polyhedral cage atoms and several of the cyclopentadienyl carbon atoms; second difference Fourier syntheses for both isomers disclosed all remaining nonhydrogen atoms. Subsequent least-squares refinement of all nonhydrogen atom positions in isomer A, with both cobalt atoms assigned anisotropic temperature factors and all other atoms assigned isotropic factors gave *R* = 0.089 and a weighted *R_w* = 0.125, where $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. Least-squares refinement of all nonhydrogen atoms in isomer B with all atoms isotropic gave *R* = 0.085 and *R_w* = 0.095. With the introduction of anisotropic temperature factors for all atoms and the application of absorption corrections, least-squares refinements through several cycles gave convergence at the *R* and *R_w* values listed in Table I, with all shift to error ratios less than 0.14. For both A and B, difference Fourier syntheses failed to reveal clear hydrogen atom positions; the largest residual peaks had heights of 0.095 and 0.102 e/Å³ in the vicinity of the cobalt atoms in A and B. These values can be compared with average peak heights of 0.4 and 0.3 e/Å³ for the boron and carbon atoms in A and B, respectively. Since NMR spectroscopic studies³⁻⁵ had established the presence of one hydrogen atom bonded to each boron and carbon atom with no bridging or other unusual hydrogen atoms present in either isomer, crystallographic determination of the hydrogen positions was considered to be of little chemical interest and was not further attempted. The error in an observation of unit weight was 2.172 for isomer A and 1.654 for isomer B.

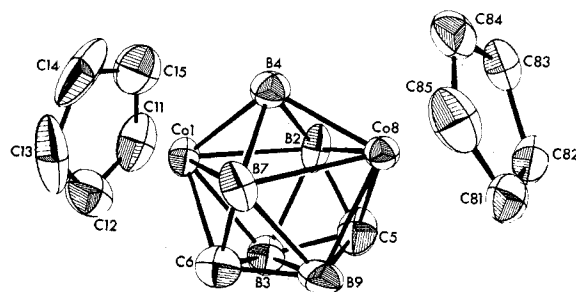


Figure 1. Molecular structure of 1,8,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇, showing nonhydrogen atoms.

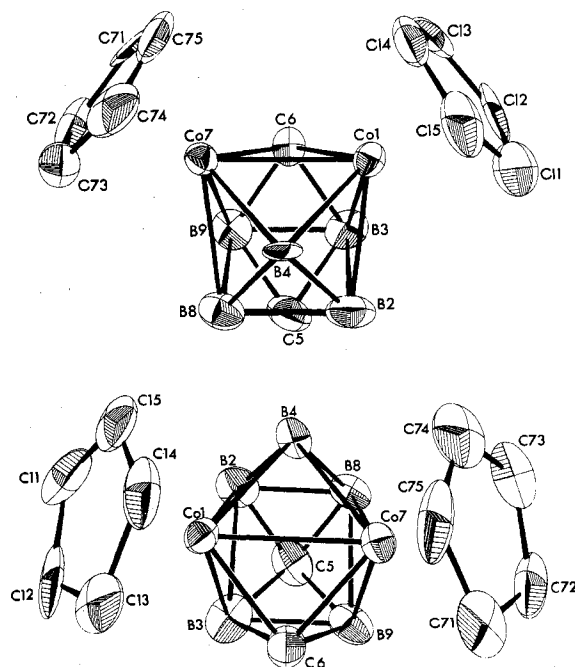


Figure 2. Two views of the molecular structure of 1,7,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇, showing nonhydrogen atoms.

No extinction correction was applied since the pattern of positive and negative deviations of observed vs. calculated intensities appeared random.

Results and Discussion

Final positional and thermal parameters for the 1,8,5,6 and

Table III. Final Positional and Thermal Parameters for 1,7,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C01	0.2019 (1)	0.1631 (3)	0.3695 (1)	0.0031 (1)	0.0143 (5)	0.0015 (1)	-0.0008 (2)	0.0004 (1)	0.0005 (1)
C07	0.3566 (1)	0.1697 (3)	0.3754 (1)	0.0033 (1)	0.0124 (5)	0.0020 (1)	0.0009 (2)	0.0007 (1)	0.0007 (1)
B2	0.279 (2)	0.392 (3)	0.144 (1)	0.007 (1)	0.014 (5)	0.0032 (6)	0.001 (2)	0.0015 (8)	0.003 (1)
B3	0.261 (1)	0.481 (3)	0.0603 (9)	0.007 (1)	0.015 (4)	0.0026 (5)	0.001 (2)	0.0003 (7)	-0.004 (1)
B4	0.233 (1)	0.539 (2)	0.1843 (8)	0.005 (1)	0.008 (3)	0.0030 (5)	0.002 (2)	0.0017 (6)	0.004 (1)
C5	0.207 (1)	0.334 (2)	0.0833 (8)	0.007 (1)	0.014 (3)	0.0038 (6)	-0.002 (2)	0.0020 (7)	0.000 (1)
C6	0.2939 (9)	0.159 (2)	0.4384 (6)	0.0039 (7)	0.022 (4)	0.0016 (3)	0.000 (2)	0.0005 (4)	0.001 (1)
B8	0.163 (1)	0.396 (2)	0.1385 (9)	0.007 (1)	0.013 (4)	0.0021 (5)	-0.001 (2)	0.0015 (7)	-0.001 (1)
B9	0.356 (1)	-0.016 (3)	0.4450 (8)	0.007 (1)	0.021 (5)	0.0019 (5)	0.001 (2)	0.0014 (6)	0.002 (1)
C11	0.071 (1)	0.160 (3)	0.331 (1)	0.006 (1)	0.031 (6)	0.0040 (7)	0.002 (2)	-0.0017 (8)	0.000 (2)
C12	0.086 (1)	0.238 (3)	0.388 (1)	0.023 (9)	0.040 (7)	0.0049 (8)	0.007 (2)	-0.0013 (7)	0.008 (2)
C13	0.141 (1)	0.386 (3)	0.3867 (9)	0.005 (1)	0.022 (5)	0.0033 (6)	0.008 (2)	-0.0004 (7)	-0.001 (1)
C14	0.156 (1)	0.392 (3)	0.328 (1)	0.003 (1)	0.026 (5)	0.0044 (7)	0.004 (2)	0.0013 (7)	0.004 (2)
C15	0.114 (1)	0.258 (3)	0.2951 (9)	0.004 (1)	0.038 (6)	0.0033 (6)	0.005 (2)	-0.0002 (7)	0.005 (2)
C71	0.432 (2)	0.382 (3)	0.402 (1)	0.008 (1)	0.020 (5)	0.0050 (8)	-0.012 (2)	0.0035 (9)	-0.004 (2)
C72	0.485 (1)	0.235 (3)	0.397 (1)	0.0032 (9)	0.033 (6)	0.0036 (7)	-0.004 (2)	0.0001 (7)	0.005 (2)
C73	0.462 (1)	0.188 (3)	0.335 (1)	0.006 (1)	0.019 (5)	0.0055 (8)	0.001 (2)	0.0030 (9)	0.002 (2)
C74	0.399 (2)	0.293 (3)	0.305 (1)	0.008 (2)	0.025 (6)	0.0044 (8)	-0.004 (2)	0.0025 (9)	0.004 (2)
C75	0.381 (1)	0.409 (3)	0.345 (1)	0.003 (1)	0.028 (6)	0.006 (1)	-0.004 (2)	0.0006 (8)	0.004 (2)

^a The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

1,7,5,6 isomers are given in Tables II and III, respectively, while bond lengths and angles are presented in Tables IV and V.

Figures 1 and 2 depict the molecular structures of the two compounds. Both molecules consist of nine-vertex tricapped trigonal-prismatic polyhedra, and the locations of cobalt, boron, and carbon atoms are in agreement with the structures proposed earlier.³⁻⁵ The carbon atoms were unequivocally located from the C-B bond lengths, which are characteristically shorter than B-B distances, and from the observation that replacement of the atomic scattering factors of carbon with those of boron, for the atoms labeled C5 and C6, produced large increases in the thermal parameters for these atoms.

All bond distances and angles in both isomers are within normal ranges for metalloboron cage systems although the interactions B7-B9 and B2-B3 in the 1,8,5,6 system are relatively long, as are the distances B8-B9 and B2-B3 in the 1,7,5,6 isomer. Each of these boron-boron bonds lies on a triangular face of the central trigonal prism and forms an edge of a four-sided face which is capped by a carbon atom; the unusual bond lengths might be attributed to withdrawal of electron density from the four-sided faces by the coordinated CH groups. Both cage systems, however, are clearly closed polyhedra and thus obey the electron-counting rules which predict closed structures (all faces triangular) for *n*-vertex cages having $2n + 2$ valence electrons involved in skeletal bonding.¹⁴

The C₅H₅ rings in both isomers are planar within one standard deviation, the dihedral angle between C₅H₅ planes being 35.4° in the 1,8,5,6 species and 100.2° in the 1,7,5,6 system. There are no close intermolecular contacts, the nearest nonhydrogen interactions being C84-C85 (3.68 Å) in the 1,8,5,6 and C11-C15 (3.76 Å) in the 1,7,5,6 isomer.

Despite the absence of crystallographic symmetry in either molecule, the 1,8,5,6 species possesses a pseudo-twofold axis passing through B4 and bisecting the B3-B9 edge. This is evident in solution, where the C₅H₅ rings rotate rapidly on the NMR time scale^{4,5} and generate equivalency between Co1 and Co8, B2 and B7, C5 and C6, and B3 and B9. Similarly, the 1,7,5,6 isomer contains a pseudomirror plane on which are located B4, C5, and C6; again, the equivalent pairs produced by this plane are seen in the ¹H and ¹¹B solution NMR spectra⁵ (in this case the cage carbon atoms are inequivalent, in contrast to the 1,8,5,6 isomer).

The most interesting aspect of these molecules is the relationship between structure and the reversible thermal mi-

gration of the cobalt atoms mentioned above. Miller and Grimes³ have suggested that the cobalt-cobalt interaction in the 1,7,5,6 isomer is sufficiently strong to account for the stability of this molecule at low or moderate temperatures; at the same time it was postulated that the shift in equilibrium in favor of the 1,8,5,6 isomer with increasing temperature may be associated with steric repulsion between the C₅H₅ groups in the 1,7,5,6 species, which would be relieved by conversion to an isomer with nonadjacent (η^5 -C₅H₅)Co moieties. Two parameters are therefore of special concern here: the cobalt-cobalt distance in the 1,7,5,6 molecule and the nearest intramolecular contact between the C₅H₅ rings in the same molecule. The Co-Co bond length of 2.444 (3) Å is of comparable magnitude to Co-Co distances in the metallocarboranes (η^5 -C₅H₅)₂Co₂C₂B₆H₈ and (η^5 -C₅H₅)₂Co₂C₂B₈H₁₀, which are respectively 2.489 (1)¹⁵ and 2.387 (2) Å,¹⁶ and also is within the range observed in (CO)₉Co₃CR-type cobalt clusters (2.43-2.55 Å).¹⁷ Differences in gross polyhedral geometry in these various systems create difficulties in attempting to draw firm conclusions about bond orders in such systems, in part because there is scarcity of relevant data and in part because the valence angle constraints of the cage structures themselves can be assumed to affect the metal-metal distances. Nevertheless, the Co-Co distance in 1,7,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇ would seem to indicate a significant bonding interaction.

A separate problem is to determine whether the C₅H₅ rings are, as suggested, sterically crowded in this molecule. The nearest intramolecular approach of carbon atoms in the two rings occurs between C14 and C75, which are separated by 3.53 Å. Assuming a nominal C-H distance of 0.95 Å, the positions of the hydrogen atoms attached to these carbon atoms are calculated to have a separation of 2.07 Å. This distance is within the sum of van der Waals radii of two hydrogen atoms, utilizing the average value of 1.2 Å for hydrogen as given by Pauling,¹⁸ and consequently offers some support for the "steric-crowding" suggestion.³ Moreover, at elevated temperatures (e.g., at 340 °C where the 1,8,5,6 \rightleftharpoons 1,7,5,6 equilibrium constant is unity³), such interactions would be substantially greater than at room temperature due to increased thermal motion of the cyclopentadienyl groups. The interaction of the C₅H₅ rings in the 1,7,5,6 isomer does not appear to be severe, which probably accounts for the small enthalpy change (-2 ± 1 kcal) involved in the isomerization. It appears, in other words, that the 1,8,5,6 \rightleftharpoons 1,7,5,6 equilibrium is a result of two moderately weak, but significant, effects—cobalt-cobalt binding and C₅H₅-C₅H₅

Table IV. Selected Distances and Angles for 1,8,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇

Distances, Å			
Co1-B4	1.960 (9)	B2-C5	1.58 (1)
Co1-C6	2.017 (9)	B2-B4	1.83 (1)
Co1-B3	2.11 (1)	B3-C6	1.52 (1)
Co1-B7	2.15 (1)	B3-C5	1.58 (1)
Co1-B2	2.156 (9)	B3-B9	1.83 (1)
Co1-C11	2.03 (1)	B4-B7	1.75 (1)
Co1-C12	2.08 (1)	C5-B9	1.52 (1)
Co1-C13	2.04 (1)	C6-B9	1.54 (1)
Co1-C14	2.03 (1)	C6-B7	1.60 (1)
Co1-C15	2.04 (1)	B7-B9	1.92 (1)
Co1-Co8	3.319 (1)	B2-B3	1.98 (1)
Co8-B4	1.915 (8)	C11-C12	1.35 (2)
Co8-C5	1.988 (9)	C12-C13	1.37 (2)
Co8-B9	2.065 (9)	C13-C14	1.39 (2)
Co8-B7	2.123 (9)	C14-C15	1.41 (2)
Co8-B2	2.216 (1)	C15-C11	1.38 (2)
Co8-C81	2.076 (7)	C81-C82	1.35 (1)
Co8-C82	2.078 (7)	C82-C83	1.42 (1)
Co8-C83	2.087 (8)	C83-C84	1.42 (1)
Co8-C84	2.057 (8)	C84-C85	1.37 (1)
Co8-C85	2.049 (9)	C85-C81	1.39 (1)

Angles, Deg			
B4-Co1-C6	89.1 (4)	B2-B4-Co1	69.3 (4)
B4-Co1-B3	93.8 (4)	Co8-B4-Co1	117.8 (5)
B4-Co1-B7	50.1 (4)	B9-C5-B2	113.6 (8)
B4-Co1-B2	52.4 (4)	B9-C5-B3	72.2 (7)
C6-Co1-B3	43.1 (4)	B9-C5-Co8	70.7 (5)
C6-Co1-B7	45.0 (4)	B2-C5-B3	77.5 (7)
C6-Co1-B2	83.4 (4)	B2-C5-Co8	73.5 (6)
B3-Co1-B7	75.5 (4)	B3-C5-Co8	117.2 (6)
B3-Co1-B2	55.2 (4)	B3-C6-B9	73.1 (8)
B7-Co1-B2	77.8 (3)	B3-C6-B7	113.8 (8)
B4-Co8-C5	90.8 (4)	B3-C6-Co1	71.8 (5)
B4-Co8-B9	93.5 (4)	B9-C6-B7	75.4 (7)
B4-Co8-B7	51.1 (4)	B9-C6-Co1	115.6 (7)
B4-Co8-B2	52.9 (4)	B7-C6-Co1	72.0 (6)
C5-Co8-B9	44.0 (5)	C6-B7-B4	112.6 (8)
C5-Co8-B7	83.9 (4)	C6-B7-B9	51.0 (6)
C5-Co8-B2	44.5 (4)	C6-B7-Co8	106.1 (6)
B9-Co8-B7	54.7 (5)	C6-B7-Co1	63.0 (5)
B9-Co8-B2	75.7 (4)	B4-B7-B9	104.1 (6)
B7-Co8-B2	78.4 (4)	B4-B7-Co8	58.3 (4)
C5-B2-B4	109.2 (7)	B4-B7-Co1	59.2 (4)
C5-B2-B3	51.3 (6)	B9-B7-Co8	61.1 (4)
C5-B2-Co1	105.8 (7)	B9-B7-Co1	95.6 (6)
C5-B2-Co8	62.0 (5)	Co8-B7-Co1	101.8 (4)
B4-B2-B3	102.8 (6)	C5-B9-C6	104.1 (8)
B4-B2-Co1	58.2 (4)	C5-B9-B3	55.4 (6)
B4-B2-Co8	56.7 (4)	C5-B9-B7	105.3 (7)
B3-B2-Co1	61.3 (4)	C5-B9-Co8	65.3 (5)
B3-B2-Co8	95.0 (5)	C6-B9-B3	52.8 (6)
Co1-B2-Co8	100.6 (4)	C6-B9-B7	53.6 (6)
C6-B3-C5	102.6 (8)	C6-B9-Co8	111.1 (7)
C6-B3-B9	54.1 (6)	B3-B9-B7	88.3 (6)
C6-B3-B2	104.4 (7)	B3-B9-Co8	103.2 (6)
C6-B3-Co1	65.1 (5)	B7-B9-Co8	64.2 (4)
C5-B3-B9	52.4 (6)	C12-C11-C15	113 (1)
C5-B3-B2	51.2 (5)	C11-C12-C13	106 (1)
C5-B3-Co1	107.7 (7)	C12-C13-C14	109 (1)
B9-B3-B2	85.8 (6)	C13-C14-C15	108 (1)
B9-B3-Co1	100.1 (6)	C11-C15-C14	104 (1)
B2-B3-Co1	63.5 (4)	C82-C81-C85	108.4 (8)
B7-B4-B2	98.1 (7)	C81-C82-C83	109.1 (8)
B7-B4-Co8	70.6 (4)	C82-C83-C84	105.6 (7)
B7-B4-Co1	70.6 (5)	C83-C84-C85	107.9 (9)
B2-B4-Co8	70.4 (4)	C81-C85-C84	109.0 (8)

repulsion—which tend in opposite directions, the latter being dominant at higher temperatures. Other factors may be operative as well but offer less satisfactory explanations for the reversible cobalt migration. For example, electrostatic repulsion between the cobalts might account for the 1,7,5,6 → 1,8,5,6 transformation, but it is not clear why this should be temperature dependent, nor does it explain the reverse (1,8,5,6 → 1,7,5,6) isomerization. Studies of additional

Table V. Selected Distances and Angles for 1,7,5,6-(η^5 -C₅H₅)₂Co₂C₂B₅H₇

Distances, Å			
Co1-C6	1.92 (1)	B2-B8	1.83 (3)
Co1-B4	2.03 (1)	B2-B3	2.01 (3)
Co1-B3	2.14 (2)	B3-C5	1.60 (3)
Co1-B2	2.18 (2)	B3-C6	1.65 (3)
Co1-Co7	2.444 (3)	B3-B9	1.85 (3)
Co1-C11	2.09 (2)	B4-B8	1.76 (3)
Co1-C12	2.06 (2)	C5-B8	1.65 (2)
Co1-C13	2.08 (2)	C5-B9	1.60 (3)
Co1-C14	2.09 (2)	C6-B9	1.68 (3)
Co1-C15	2.11 (2)	B8-B9	2.01 (3)
Co7-C6	1.93 (1)	C11-C12	1.41 (3)
Co7-B4	2.04 (2)	C12-C13	1.46 (3)
Co7-B9	2.17 (2)	C13-C14	1.42 (3)
Co7-B8	2.19 (2)	C14-C15	1.39 (3)
Co7-C71	2.07 (2)	C15-C11	1.41 (3)
Co7-C72	2.07 (2)	C71-C72	1.46 (3)
Co7-C73	2.09 (2)	C72-C73	1.44 (3)
Co7-C74	2.11 (2)	C73-C74	1.37 (3)
Co7-C75	2.07 (2)	C74-C75	1.36 (3)
B2-C5	1.67 (3)	C75-C71	1.40 (3)
B2-B4	1.75 (3)		

Angles, Deg			
C6-Co1-B4	95.5 (7)	B8-B4-Co7	69.9 (9)
C6-Co1-B3	47.5 (7)	Co1-B4-Co7	73.8 (5)
C6-Co1-B2	89.6 (8)	B3-C5-B9	71 (1)
C6-Co1-Co7	50.9 (4)	B3-C5-B8	113 (1)
B4-Co1-B3	92.7 (8)	B3-C5-B2	76 (1)
B4-Co1-B2	48.8 (8)	B9-C5-B8	76 (1)
B4-Co1-Co7	53.2 (5)	B9-C5-B2	114 (2)
B3-Co1-B2	55.3 (9)	B8-C5-B2	67 (1)
B3-Co1-Co7	82.0 (6)	B3-C6-B9	68 (1)
B2-Co1-Co7	81.9 (6)	B3-C6-Co1	73.4 (9)
C6-Co7-B4	94.9 (7)	B3-C6-Co7	114 (1)
C6-Co7-B9	48.0 (7)	B9-C6-Co1	115 (1)
C6-Co7-B8	89.1 (8)	B9-C6-Co7	73.2 (8)
C6-Co7-Co1	50.4 (4)	Co1-C6-Co7	78.7 (5)
B4-Co7-B9	92.8 (8)	C5-B8-B4	109 (1)
B4-Co7-B8	49.1 (7)	C5-B8-B2	57 (1)
B4-Co7-Co1	53.0 (5)	C5-B8-B9	51 (1)
B9-Co7-B8	54.9 (8)	C5-B8-Co7	104 (1)
B9-Co7-Co1	82.3 (6)	B4-B8-B2	58 (1)
B8-Co7-Co1	81.8 (6)	B4-B8-B9	108 (1)
C5-B2-B4	110 (2)	B4-B8-Co7	61.0 (8)
C5-B2-B8	56 (1)	B2-B8-B9	91 (1)
C5-B2-B3	51 (1)	B2-B8-Co7	98 (1)
C5-B2-Co1	104 (1)	B9-B8-Co7	62.0 (8)
B4-B2-B8	59 (1)	C5-B9-C6	105 (1)
B4-B2-B3	107 (1)	C5-B9-B3	55 (1)
B4-B2-Co1	61.2 (8)	C5-B9-B8	53 (1)
B8-B2-B3	90 (1)	C5-B9-Co7	107 (1)
B8-B2-Co1	98 (1)	C6-B9-B3	55 (1)
B3-B2-Co1	61.5 (8)	C6-B9-B8	103 (1)
C5-B3-C6	106 (1)	C6-B9-Co7	58 (7)
C5-B3-B9	55 (1)	B3-B9-B8	89 (1)
C5-B3-B2	54 (1)	B3-B9-Co7	97 (1)
C5-B3-Co1	108 (1)	B8-B9-Co7	63.1 (8)
C6-B3-B9	57 (1)	C12-C11-C15	107 (2)
C6-B3-B2	104 (1)	C11-C12-C13	109 (2)
C6-B3-Co1	59.1 (7)	C12-C13-C14	105 (2)
B9-B3-B2	90 (1)	C13-C14-C15	110 (2)
B9-B3-Co1	99 (1)	C11-C15-C14	109 (2)
B2-B3-Co1	63.2 (8)	C72-C71-C75	105 (2)
B2-B4-B8	63 (1)	C71-C72-C73	105 (2)
B2-B4-Co1	70.0 (9)	C72-C73-C74	110 (2)
B2-B4-Co7	107 (1)	C73-C74-C75	107 (2)
B8-B4-Co1	106 (1)	C71-C75-C74	112 (2)

systems involving reversible interconversion of metallo-carboranes may help to place this unusual type of boron cage rearrangement in better perspective.

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Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of 2,3,7,8,12,13,17,18-Octaethylporphinatooxovanadium(IV)

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The structure of 2,3,7,8,12,13,17,18-octaethylporphinatooxovanadium(IV) has been determined from three-dimensional x-ray diffraction data. The complex crystallizes in the monoclinic space group $C_{2h}^5-P2_1/c$ with four molecules in a unit cell of dimensions $a = 14.334$ (3), $b = 23.061$ (8), $c = 9.815$ (2) Å, $\beta = 104.18$ (2)°. The structure was solved by direct methods. Least-squares refinement has led to a final value of the conventional R index (on F_o^2) of 0.084 based on 6482 reflections (including $F_o^2 \leq 0$). The vanadium atom is found to be 0.543 Å above the plane of the four nitrogen atoms. The average V–N bond distance is 2.102 (6) and the V–O bond length is 1.620 (2) Å. The porphyrin itself is slightly nonplanar.

Introduction

In recent years a considerable amount of interest has been devoted to synthetic models for various biological systems.¹ Although vanadyl porphyrins are not known to be involved in any biological processes, they do occur in Nature.² Vanadyl porphyrins have been found in oil deposits, various bitumens, and even meteorites.³ The source of the vanadyl porphyrin in meteorites has been proposed to be some abiological synthesis.³ Vanadium has been found in blood cells of certain ascidians, but the mode of bonding to the protein is not understood.⁴ The degradation of chlorophyll and other biologically active porphyrins is thought to be the source of vanadyl porphyrins in petroleum.^{3,5} The porphyrin which is commonly found in petroleum has been identified as an analogue of etioporphyrin I (Figure 1). Since 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) is a close synthetic model for these natural porphyrins, the structure of VO(OEP) has been determined and is reported here. The structure is compared with that of vanadyl deoxyphylloerythroetioporphyrin, which is a model for chlorophyll. This is the only other vanadyl porphyrin whose structure has been determined.

Experimental Section

A sample of VO(OEP) was kindly supplied by Professor H. H. Inhoffen. Suitable crystals, deep red in color, were obtained by slow

evaporation from a chloroform–toluene solution. Preliminary Weissenberg photographs, showed monoclinic symmetry and systematic absences ($0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$) consistent with space group $C_{2h}^5-P2_1/c$.

The crystal selected for data collection was a monoclinic prism with bounding faces of the forms $\{101\}$, $\{011\}$, $\{100\}$, and $\{010\}$. Approximate dimensions of the crystal are $0.207 \times 0.221 \times 0.162$ mm. The calculated volume is 0.0066 mm³. The crystal was mounted with the $[100]$ direction approximately along the spindle axis.

The lattice parameters, obtained as previously described^{6,7} by hand centering of 13 reflections in the range $40 < 2\theta < 60^\circ$ on a Picker four-circle automatic diffractometer using Cu $K\alpha_1$ radiation (λ 1.540 562 Å), are $a = 14.334$ (3), $b = 23.061$ (8), $c = 9.815$ (2) Å, $\beta = 104.18$ (2)°. The calculated density, based on four molecules per unit cell, of 1.269 g/cm³ agrees well with the value of 1.25 (1) g/cm³ measured by flotation in aqueous zinc chloride solution.

Data were collected in shells of 2θ for $5 < 2\theta < 160^\circ$ by the θ – 2θ scan method using Cu $K\alpha$ radiation prefiltered with Ni foil. The scan range in 2θ was from 0.80° below the Cu $K\alpha_1$ peak to 0.80° above the Cu $K\alpha_2$ peak. The takeoff angle was 3.0° and the scintillation counter was positioned 32 cm from the crystal preceded by an aperture 3.1 mm high by 3.1 mm wide. The pulse height analyzer was set to admit about 90% of the Cu $K\alpha$ peak. Background counts were taken for 10 s at each end of the scan range and a scan rate of 2° in 2θ per minute was used. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts/s during a scan. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured