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Crystal and Molecular Structure of 1,5'-Bidecaboran(14)yl: A New Borane from γ Irradiation of Decaborane(14)[1]

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The previously unknown structure of the most abundant of several isomers $B_{20}H_{26}$ produced by γ irradiation of decaborane(14) has been determined by X-ray crystal-structure analysis. The molecule, named 1,5'-bidecaboran(14)yl, is made up of a 1-decaboran(14)yl group linked by a two-center B–B bond to a 5-decaboran(14)yl group. The linking B1–B'5 bond, a type for which no previous precise metrical data exist, has a length of 1.698 (3) Å. The interatomic distances and angles in the decaboranyl groups, after correction for the effects of thermal motion, agree remarkably well with the corresponding ones in decaborane(14) known from analysis of low-temperature neutron-diffraction data. Most of the larger differences are for distances and angles involving atoms B1 and B'5 of the connecting link. Crystallographic data: monoclinic, space group $P2_1/n$, a = 7.235 (1) Å, b = 15.453 (4) Å, c = 14.895 (3) Å, β = 91.42 (2)°, 4 formula units per cell, d_{calcd} = 0.967 g/cm^3 [λ(Cu Kα) 1.5418 Å].

The preparation by γ irradiation of decaborane(14) and the partial characterization of eight isomeric boranes of empirical formula $B_{20}H_{26}$ are described elsewhere by Pinson, Ingram, and Brown.[3] Each of the isomers was presumed to be made up of two of the various moieties $B_{10}H_{13}$ theoretically producible by abstraction of a single hydrogen atom from the decaborane(14) molecule. The isomer whose structure is described here is the most abundant one, accounting for 70% of the total irradiation product. Its infrared spectrum suggested molecular asymmetry. It was the only one for which crystals had been grown at the time the X-ray work was started.

Experimental Section

Unit Cell and Space Group. Only two single crystals large enough to be used were available. These were colorless, cloudy crystals of rather poor quality, grown by evaporation of solvent from a solution of the compound in cyclohexane. The smaller of the two crystals was used to make precession photographs, from which the space group was established as $P2_1/n$[4] (systematic absences: $h0l$ for $h + l$ odd and $0k0$ for k odd) and approximate cell parameters were obtained. Precise values for the cell parameters were derived by the method of least squares[5] from angle data for reflections from the second crystal recorded at 21–22 °C with the Oak Ridge computer-controlled diffractometer.[6] Data for 28 reflections in the range 11–85° in 2θ for Cu Kα radiation (unresolved doublet, λ 1.5418 Å) yielded the following parameters (and standard errors in parentheses): a = 7.235 (1) Å, b = 15.453 (4) Å, c = 14.895 (3) Å, β = 91.42 (2)°. The reasonable density 0.967 g/cm^3 was calculated on the assumption of four $B_{20}H_{26}$ formula units per cell.

Reflection Data. The crystal used in collecting the intensity data was the second and larger of the two available. With dimensions about 0.15 × 0.35 × 0.7 mm, it was somewhat longer than optimum for the 0.5-mm aperture of the collimator, but we were afraid to attempt to trim it for fear of losing it. We also needed all the intensity we could get, even at the risk of having slightly less accurate measurements.

The crystal was far from an ideal specimen. The effective mosaic spreads were about 2.7° and 1.7° (full width at background, allowing for partial splitting) for reflection vectors approximately perpendicular and parallel, respectively, to the ϕ axis, which was ~3° from the **a*** direction. To achieve proper integration of the reflection intensities, it was necessary to use the triple ω-scan technique[7] as was used with a hexachlorobenzene crystal[8] of similar mosaicity. In this somewhat unusual procedure the height (dimension parallel to the 2θ axis) of the receiving aperture was set at the maximum, corresponding to an acceptance angle of 1.8°, and the width of the aperture was set by calculation as described by Einstein[7] to angles from 0.9 to 1.8° depending upon the particular 2θ range being recorded. The takeoff angle was 1.5°. The ω-scan range was 3.5°, and the step width was 0.05°. The counting time was 4 s at each point in the main scan and 2 s at each point in each background scan. The radiation was Cu Kα, unfiltered below 45° in 2θ and filtered through nickel foil above 45°. It was shown by varying the slit widths for selected reflections that no significant intensity was being excluded by the slits.

Over a period of about 6 weeks, 2953 intensities, representing 2663 independent reflections, were recorded at 21–22 °C with the automatic diffractometer to the limit 125° in 2θ. Data recorded regularly every 50 observations for three reference reflections showed an average 2% decline of intensity over the course of the data taking, indicating slight deterioration from effects of the X radiation or from contact with the air. From the raw intensity data and corresponding standard errors, the structure-factor squares, F_o^2, were calculated in the usual preliminary data processing,[9] along with standard errors, $\sigma(F_o^2)$, with corrections for the deterioration and for absorption and with averaging of the small number of replicate and equivalent reflections. The value of the absorption coefficient used was 1.89 cm^{-1}; the absorption

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Table I. Fractional Coordinates *x, y, z* and Thermal Parameters U_{ij} (Å^2) of the Boron Atoms in 1,5′-Bidecaboran(14)yl[a]

atom	10^5x	10^5y	10^5z	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
B1	12949 (26)	41842 (12)	34114 (14)	393 (11)	351 (10)	530 (13)	22 (9)	11 (9)	−26 (9)
B2	−4867 (33)	45612 (15)	26539 (17)	475 (13)	477 (13)	678 (16)	−30 (11)	−70 (12)	77 (12)
B3	2988 (35)	52338 (13)	35461 (17)	596 (15)	370 (11)	649 (16)	70 (11)	117 (12)	34 (11)
B4	26278 (36)	50467 (14)	39034 (19)	629 (15)	450 (13)	585 (16)	−112 (11)	−50 (13)	17 (11)
B5	15146 (35)	40397 (16)	22538 (17)	658 (15)	392 (12)	584 (15)	−40 (11)	36 (12)	−31 (12)
B6	3896 (44)	49054 (18)	16586 (20)	723 (19)	536 (16)	620 (18)	−95 (14)	−136 (15)	55 (13)
B7	−891 (38)	56918 (16)	24915 (19)	596 (15)	497 (14)	772 (18)	64 (12)	39 (14)	134 (13)
B8	19877 (40)	60080 (16)	33132 (18)	809 (18)	396 (13)	647 (16)	−68 (12)	58 (14)	−30 (12)
B9	41378 (42)	54811 (20)	31535 (20)	620 (17)	565 (16)	745 (18)	−153 (15)	−72 (14)	97 (15)
B10	35719 (32)	43593 (17)	30757 (17)	446 (13)	523 (14)	717 (16)	−7 (11)	40 (12)	84 (12)
B′1	22266 (34)	23259 (14)	39766 (17)	561 (14)	359 (11)	621 (16)	63 (10)	95 (12)	6 (11)
B′2	−1478 (36)	22846 (15)	36511 (18)	661 (15)	424 (12)	570 (15)	−89 (11)	−58 (13)	−24 (12)
B′3	8477 (35)	14364 (15)	43077 (17)	785 (17)	358 (12)	632 (15)	−7 (11)	115 (13)	−9 (11)
B′4	27569 (35)	17565 (16)	49879 (18)	593 (15)	505 (14)	757 (17)	109 (12)	1 (13)	149 (13)
B′5	9113 (29)	32767 (14)	40189 (15)	400 (11)	396 (11)	514 (13)	14 (9)	5 (10)	−33 (9)
B′6	−14202 (35)	29585 (17)	42991 (18)	395 (13)	601 (15)	692 (17)	−30 (12)	−15 (12)	90 (13)
B′7	−13215 (36)	18394 (18)	45843 (20)	590 (15)	574 (16)	810 (19)	−133 (13)	−25 (14)	117 (14)
B′8	5944 (39)	14762 (17)	54579 (18)	785 (18)	462 (14)	684 (17)	60 (13)	117 (14)	64 (14)
B′9	20885 (44)	23174 (19)	58951 (21)	768 (19)	611 (16)	743 (20)	111 (15)	−132 (16)	85 (14)
B′10	28326 (37)	29076 (16)	49353 (19)	482 (14)	511 (14)	685 (17)	32 (12)	−79 (13)	21 (12)

[a] See text for the form of the temperature factor. The numbers in parentheses, corresponding to the least significant digits of the adjacent parameters, are the estimated standard errors.

Table II. Fractional Coordinates of the Hydrogen Atoms in 1,5′-Bidecaboran(14)yl[a]

atom	10^4x	10^4y	10^4z
H2	−1892 (24)	4283 (12)	2684 (12)
H3	−738 (23)	5417 (12)	4078 (13)
H4	2950 (29)	5039 (12)	4653 (14)
H5	1583 (27)	3409 (11)	1938 (11)
H5–6	2002 (28)	4568 (11)	1654 (11)
H6	−161 (32)	4867 (13)	954 (16)
H7	−1147 (27)	6215 (14)	2377 (15)
H7–6	963 (27)	5704 (13)	1816 (13)
H8	1961 (31)	6672 (11)	3583 (13)
H8–9	3143 (27)	5995 (12)	2690 (16)
H9	5525 (24)	5769 (13)	3252 (14)
H10	4697 (23)	3880 (12)	3153 (14)
H10–9	4161 (25)	4911 (12)	2520 (15)
H′1	3282 (27)	2311 (10)	3467 (13)
H′2	−555 (30)	2146 (11)	2932 (16)
H′3	901 (31)	773 (11)	4037 (13)
H′4	3994 (27)	1342 (13)	4990 (15)
H′5–6	−171 (28)	3463 (13)	4632 (14)
H′6	−2706 (24)	3323 (13)	4152 (13)
H′7	−2621 (29)	1460 (14)	4588 (16)
H′7–6	−1697 (21)	2457 (10)	5096 (11)
H′8	296 (26)	917 (11)	5911 (12)
H′8–9	262 (30)	2131 (14)	5929 (14)
H′9	2662 (38)	2396 (15)	6652 (15)
H′10	4071 (27)	3330 (12)	5008 (12)
H′10–9	1818 (25)	3118 (12)	5549 (14)

[a] The numbers in the atom symbols indicate the boron atoms to which the hydrogen atoms are attached.

correction factors[10] on the observed intensities ranged only from 1.033 to 1.080. Retained in the data set were 175 slightly negative F_o^2 values, resulting from statistical fluctuations and instrumental errors. The standard errors were obtained after the variances of the F_o^2 data were corrected empirically by the addition of the term $(0.03F_o^2)^2$ to each variance from counting statistics.[11] The weights used later in least-squares refinement with the F_o^2 values as observations were the reciprocals of these corrected variances. The reflection data were put on an approximately absolute scale, and the normalized structure factors,[12] *E*'s, were computed with the program ORESTES.[13]

Structure Solution and Refinement. After preliminary, but not exhaustive, attempts at solution with the more sophisticated program MULTAN[14] failed, the solution for the structure was obtained through use of Long's multisolution direct method[15] based on iterative use of the Σ_2 relation.[12] All 20 of the boron atoms in the asymmetric unit were identifiable as the 20 highest peaks in the *E* map[16] computed[17] with the "best" sign combination for the 356 *E* values of magnitude ≥1.50.

After some preliminary cycles of least-squares refinement,[18] all of the 26 hydrogen atoms were located in a difference map, and their parameters were thereafter refined along with those of the boron atoms. In the final full-matrix least-squares cycles, three coordinates and six anisotropic thermal parameters were adjusted for each of the 46 B and H atoms along with a single scale factor on F_c, making a total of 415 parameters adjusted. The final measures of goodness of fit[19] are $R(F) = 0.059$, $R(F^2) = 0.074$, $R_w(F^2) = 0.114$, and $\sigma_1 = 2.313$. In these final cycles the 18 reflections with $2\theta \leq 20°$ were given zero weights because their lower backgrounds were considered inaccurately measured; the 416 reflections having $F_c^2 \leq \sigma(F_o^2)$ were also omitted as of uncertain phase. In the last cycle no parameter shift was greater than one-fourth of the corresponding standard error. The boron scattering factors used were from the tabulation of Cromer and Waber[20] and those for hydrogen were from Stewart et al.[21]

Application of the *R*-factor ratio test[22,23] showed that the improvement in agreement resulting from use of the anisotropic thermal parameters for the hydrogen atoms is highly significant. The experimental ratio of $R_w(F^2)$ values for the refinements with isotropic and anisotropic hydrogen thermal parameters is $\mathcal{R} = 1.129$, to be compared with the considerably smaller value of 1.051 for $\mathcal{R}_{130,1714,0.005}$ interpolated for the 0.005 probability point from a table of significance points of $\mathcal{R}$.[23]

A final difference map showed no interpretable density, the excursions ranging only from −0.22 to +0.15 e/Å^3. A partial difference map using the final phase signs but not including the hydrogen atoms in the $|F_c|$ values showed the 26 hydrogen atoms as the first 26 peaks, with densities from 0.75 down to 0.49 e/Å^3. The next lower peak had a density of 0.17 e/Å^3. In a final Fourier map the 20 peaks representing the boron atoms had densities from 4.7 to 6.2 e/Å^3.

Table I gives for the boron atoms the final values of the fractional coordinates and of the coefficients U_{ij} (Å^2) of the temperature-factor expression $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2klb^*c^*U_{23})]$. For the hydrogen atoms, fractional coordinates are given in Table II and thermal parameters in the supplementary material.[24] The latter material also includes a listing of observed and calculated structure factors.

Discussion

Structure. The geometry of the molecule and the packing of the molecules are shown in the stereoscopic drawings of Figures 1 and 2, prepared with the program ORTEP.[25] Molecular structural details are tabulated as follows: Table III, B–B distances; Table IV, B–B–B angles; Table V, apparent B–H distances; and in the supplementary material,[24] angles H–B–H and H–B–B. The grouping and averaging of parameters within each table are designed to facilitate comparison with corresponding average molecular parameters of decaborane(14) from neutron-diffraction analysis[26,27] and to show the perturbing effects of the B–B link between the two $B_{10}H_{13}$ moieties. The average parameters for $B_{10}H_{14}$ included in the tables are from the refinement of Brill et al.,[27] who used

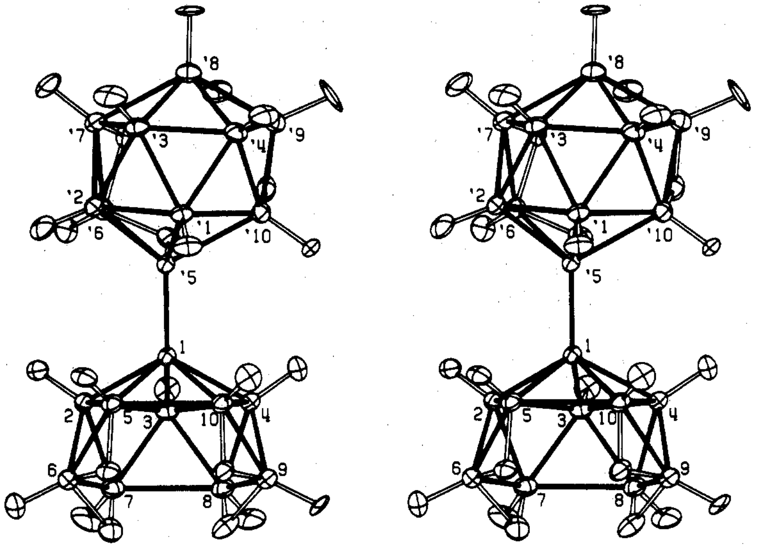

Figure 1. Stereoscopic view of the 1,5′-bidecaboran(14)yl molecule showing the thermal ellipsoids of 10% probability.[25] Only the boron atoms are numbered, and the boron skeleton is emphasized by the black "sticks" connecting the boron atoms.

the data of Tippe and Hamilton[26] and corrected the latter authors' errors of including some incorrect symmetry operations and not adjusting some properly refinable parameters. Generally, the groups in the tables correspond to groups of equivalent parameters in the isolated $B_{10}H_{14}$ molecule (point-group symmetry *mm*2).

All of the $B_{20}H_{26}$ distances in Table III and nearly all of the angles in Table IV are values that have been corrected for the effects of thermal motion[28] from the results of a segmented-body analysis (see below). Each parameter that has been corrected has next to it within angle brackets ⟨⟩ the additive correction that it includes. The corrections should in principle make the comparison of X-ray and neutron results more meaningful, since the latter are based on data recorded at −160 °C, where thermal motion is greatly reduced. The standard errors quoted in the tables for the distances and angles in $B_{20}H_{26}$ were calculated[29] by using the full least-squares covariance matrix.

In square brackets below each average in the tables is the root-mean-square deviation from the average. Since $B_{20}H_{26}$ has no symmetry and $B_{10}H_{14}$ has point-group symmetry 2 in the crystal, there are generally more contributors to an average for $B_{20}H_{26}$ than for the corresponding one for $B_{10}H_{14}$.

Since the structure was previously unknown, its aspect of prime chemical interest is the atom connectivity, i.e., the molecular topology. As shown in the stereoscopic drawing of Figure 1, two decaboran(14)yl groups of formula $B_{10}H_{13}$ are connected to each other by a two center B–B bond, from B1 in the unprimed group to B′5 in the primed group. The resulting molecule, $B_{20}H_{26}$, is unsymmetrical, as was suggested by the infrared spectrum;[3] it is therefore named 1,5′-bidecaboran(14)yl, in accordance with IUPAC conventions.[30]

The two-center linking bond B1–B′5 has the length 1.698 (3) Å, at the lower end of the normal B–B distance range. This is the first precise (presumably accurate) metrical datum for such a bond. The only other datum is the value 1.74 ± 0.06 Å given by Grimes et al.[31] from a two-dimensional X-ray structure analysis of 1,1′-$(B_5H_8)_2$, a decaborane(16) isomer. Probably the other isomers of $B_{20}H_{26}$[3] also have B–B two-center links. There are three other boranes for which such B–B links between boranyl groups are inferred from NMR studied. Two of these are the isomers 1,2′-$(B_5H_8)_2$[32] and 2,2′-$(B_5H_8)_2$[32–34] of decaborane(16); the third is 2,2′-$(B_4H_9)_2$, or octaborane(18).[33]

Table III. Individual and Group-Average B-B Distances (Å, Corrected for Thermal Motion) in 1,5′-Bidecaboran(14)yl and Comparison with Corresponding Distances in Decaborane(14) from Low-Temperature Neutron-Diffraction Analysis

atom pair	$B_{20}H_{26}$[a] unprimed half	primed half	average[c]	$B_{10}H_{14}$[b] average[c]
B1–B′5	1.698 ⟨02⟩		1.698 ⟨02⟩	
B1–B2	1.798 ⟨09⟩	1.787 ⟨12⟩		
B1–B4	1.799 ⟨08⟩	1.784 ⟨06⟩		
B3–B2	1.780 ⟨10⟩	1.783 ⟨06⟩	1.787 ⟨10⟩	1.785
B3–B4	1.789 ⟨11⟩	1.776 ⟨13⟩	[0.008]	[0.001]
B1–B3	1.796 ⟨08⟩	1.781 ⟨06⟩	1.789 ⟨07⟩ [0.008]	1.776 [0.004]
B1–B5	1.757 ⟨07⟩	1.759 ⟨06⟩		
B1–B10	1.762 ⟨08⟩	1.745 ⟨11⟩		
B3–B7	1.744 ⟨05⟩	1.757 ⟨10⟩	1.752 ⟨07⟩	1.751
B3–B8	1.755 ⟨04⟩	1.737 ⟨08⟩	[0.008]	[0.002]
B2–B6	1.715 ⟨04⟩	1.714 ⟨09⟩	1.712 ⟨07⟩	1.732
B4–B9	1.722 ⟨04⟩	1.695 ⟨09⟩	[0.010]	[0.001]
B2–B5	1.783 ⟨10⟩	1.803 ⟨09⟩		
B2–B7	1.791 ⟨03⟩	1.791 ⟨06⟩		
B4–B8	1.785 ⟨04⟩	1.792 ⟨09⟩	1.790 ⟨07⟩	1.790
B4–B10	1.786 ⟨09⟩	1.786 ⟨05⟩	[0.006]	[0.003]
B5–B10	1.978 ⟨11⟩	2.018 ⟨11⟩	1.989 ⟨11⟩	1.987
B7–B8	1.987 ⟨11⟩	1.971 ⟨11⟩	[0.018]	[0.002]
B5–B6	1.795 ⟨06⟩	1.826 ⟨10⟩		
B7–B6	1.787 ⟨10⟩	1.786 ⟨04⟩		
B8–B9	1.787 ⟨10⟩	1.813 ⟨11⟩	1.797 ⟨07⟩	1.787
B10–B9	1.789 ⟨05⟩	1.795 ⟨05⟩	[0.014]	[0.005]

[a] Each number in angle brackets ⟨⟩, corresponding to the least significant digits of the adjacent distance, gives the additive correction for thermal motion included in the distance. The esd's of the individual distances in $B_{20}H_{26}$ are 0.003–0.004 Å. [b] See Brill et al.[27] The esd's of the individual distances in $B_{10}H_{14}$ are 0.003–0.007 Å. [c] In square brackets under each average distance is the root-mean-square deviation from the average. See the text for an explanation of the grouping for the averaging.

In Tables III and IV the comparable averages for $B_{20}H_{26}$ and $B_{10}H_{14}$ agree remarkably well, and in $B_{20}H_{26}$, as expected, most of the larger deviations from the averages are for distances and angles involving the linking atoms B1 and B′5. All of the distances within the unprimed moiety involving atom B1 and all those in the primed moiety involving B′5 are at least slightly longer than their respective group averages and longer than the corresponding averages for $B_{10}H_{14}$, suggesting that the B–B link replacing two B–H terminal bonds is formed at the expense of slight weakening of the neighboring bonds. The

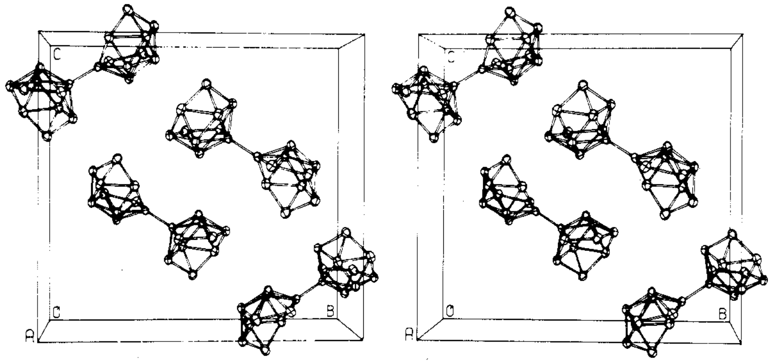

Figure 2. Stereoscopic view showing the packing of molecules in the 1,5′-bidecaboran(14)yl crystal. Boron atoms are represented by their thermal ellipsoids of 10% probability;[25] hydrogen atoms are not shown.

Table IV. Individual and Group-Average B–B–B Angles (Deg, Corrected[a] for Thermal Motion) in 1,5′-Bidecaboran(14)yl and Comparison with Corresponding Angles in Decaborane(14) from Low-Temperature Neutron-Diffraction Analysis

	$B_{20}H_{26}$[a]			$B_{10}H_{14}$[b]
ATOM TRIPLE	UNPRIMED HALF	PRIMED HALF	AVG.[c]	AVG.[c]
B2 B1 B'5	118.8			
B4 B1 B'5	119.4		119.1 [0.3]	118.1[d] [0.2]
B3 B1 B'5	128.2			127.9[d] [0.2]
B5 B1 B'5	116.1			
B10 B1 B'5	116.5		116.3 [0.2]	114.8[d] [0.1]
B1 B'5 B'1	125.3			122.7[d] [0.4]
B1 B'5 B'2	128.2			126.4[d] [0.2]
B1 B'5 B'6	120.8			119.7[d] [0.2]
B1 B'5 B'10	118.6			116.7[d] [0.2]
B2 B1 B5	60.2<1>	61.1<$\underline{0}$>		
B4 B1 B10	60.2<1>	60.8<$\bar{1}$>		
B2 B3 B7	61.1<$\bar{2}$>	60.8<0>		
B4 B3 B8	60.5<$\bar{1}$>	61.3<$\bar{1}$>	60.8<0> [0.5]	60.8 [0.1]
B3 B1 B2	59.4<1>	60.0<$\bar{1}$>		
B3 B1 B4	59.7<1>	59.8<3>		
B1 B3 B2	60.4<0>	60.2<3>		
B1 B3 B4	60.3<0>	60.2<0>	60.0<1> [0.3]	60.2 [0.1]
B5 B1 B10	68.4<1>	70.3<0>		
B7 B3 B8	69.2<2>	68.7<1>	69.2<1> [0.7]	69.1 [0.1]
B1 B2 B3	60.3<0>	59.9<$\bar{1}$>		
B1 B4 B3	60.1<0>	60.1<$\bar{1}$>	60.1<$\bar{1}$> [0.1]	59.7 [0.1]
B1 B2 B5	58.8<0>	58.7<$\bar{1}$>		
B3 B2 B7	58.5<0>	58.9<1>		
B1 B4 B10	58.9<$\underline{0}$>	58.5<2>		
B3 B4 B8	58.8<$\bar{1}$>	58.3<0>	58.7<0> [0.2]	58.7 [0.1]
B6 B2 B5	61.7<$\bar{1}$>	62.5<$\underline{0}$>		
B6 B2 B7	61.2<2>	61.2<$\bar{2}$>		
B9 B4 B8	61.3<$\underline{3}$>	62.6<$\underline{1}$>		
B9 B4 B10	61.3<$\bar{1}$>	62.0<$\bar{1}$>	61.7<0> [0.5]	61.0 [0.1]
B1 B5 B2	61.0<0>	60.2<$\underline{2}$>		
B3 B7 B2	60.4<2>	60.3<$\bar{1}$>		
B3 B8 B4	60.7<$\underline{3}$>	60.4<1>		
B1 B10 B4	60.9<$\bar{1}$>	60.7<0>	60.6<1> [0.3]	60.5 [0.1]
B1 B5 B10	55.9<$\bar{1}$>	54.5<0>		
B3 B7 B8	55.7<$\bar{1}$>	55.2<0>		
B3 B8 B7	55.1<$\bar{2}$>	56.2<$\underline{1}$>		
B1 B10 B5	55.7<$\bar{1}$>	55.2<$\bar{1}$>	55.4<$\bar{1}$> [0.5]	55.5 [0.2]
B6 B5 B2	57.3<$\bar{1}$>	56.4<0>		
B6 B7 B2	57.3<$\bar{1}$>	57.3<2>		
B9 B8 B4	57.6<$\bar{1}$>	56.1<0>		
B9 B10 B4	57.6<$\bar{1}$>	56.5<1>	57.0<0> [0.5]	57.9 [0.1]
B10 B5 B6	116.8<1>	113.7<$\underline{2}$>		
B8 B7 B6	116.3<0>	117.2<$\bar{2}$>		
B7 B8 B9	117.3<0>	116.4<$\underline{2}$>		
B5 B10 B9	117.0<0>	118.0<$\bar{1}$>	116.6<0> [1.2]	116.7 [0.1]
B2 B6 B5	61.0<$\underline{2}$>	61.1<$\bar{1}$>		
B2 B6 B7	61.5<$\bar{1}$>	61.5<$\underline{0}$>		
B4 B9 B8	61.1<$\bar{2}$>	61.3<$\bar{1}$>		
B4 B9 B10	61.1<2>	61.5<$\bar{1}$>	61.3<0> [0.2]	61.1 [0.0]
B5 B6 B7	105.0<0>	106.5<$\bar{1}$>		
B8 B9 B10	104.7<0>	105.4<$\bar{2}$>	105.4<$\bar{1}$> [0.7]	104.8 [0.0]

[a] Corrections were made except for the angles involving boron atoms from both halves of the molecule. As for the distance corrections in Table III, the additive corrections included in the angles are specified by the numbers in angle brackets. The esd's of the individual angles are 0.1–0.2°. [b] See ref 27, where esd's from 0.1 to 0.2° are also reported for $B_{10}H_{14}$. [c] In square brackets under each average angle is the root-mean-square deviation from the average. [d] These are for angles B–B–H corresponding to the B–B–B′ and B–B′–B′ angles in $B_{20}H_{26}$. The esd's reported for these are 0.2–0.3°.

distances B′5–B′10 and B′5–B′6 at 2.018 (3) and 1.826 (3) Å are notably different from the corresponding distances in $B_{10}H_{14}$; the B′5–B′10 distance is at the upper end of the known B–B distance range in boranes.

For reasons not clear, the distances B′4–B′9, B′8–B′9, and B′3–B′8 all appear significantly different from the corresponding averages in $B_{10}H_{14}$, though they would hardly be expected to be affected at all by the intermoiety link. Although in $B_{20}H_{26}$ the B′4–B′9 distance stands out as notably discrepant, the group average without it is 1.717 Å, still lower than the average 1.732 Å for $B_{10}H_{14}$. The difference is probably related to the fact that we are comparing a distance derived from X-ray data with another derived from neutron data. Brill et al,[27] in deducing the distribution of bonding electrons in $B_{10}H_{14}$ from X-ray data by using the atomic parameters from neutron data, concluded that there is a charge of 0.7 e centered nearly on the B2–B6 line at ~0.6 Å from B6. Refining the charge distribution, using the same data, Dietrich and Scheringer[36] placed a charge of 1.02 e at 0.77 Å from B6. In $B_{20}H_{26}$ one would expect similar charges asymmetrically located along the lines B2–B6, B4–B9, and their primed counterparts. The asymmetry would be expected

Table V. Apparent B-H Distances (Å, Uncorrected) in 1,5′-Bidecaboran(14)yl and Comparison with Corresponding Distances in Decaborane(14) from Low-Temperature Neutron-Diffraction Analysis

	$B_{20}H_{26}$[a,c]		
atom pair	unprimed half	primed half	$B_{10}H_{14}$[b,c]
B1–H1		1.09	
B2–H2	1.11	1.13	
B3–H3	1.14	1.10	
B4–H4	1.14	1.10	
B5–H5	1.08		
B6–H6	1.12	1.11	
B7–H7	1.12	1.11	
B8–H8	1.10	1.12	
B9–H9	1.10	1.20	
B10–H10	1.10	1.11	
av	1.12 [3]		1.186 [5]
B5–H5–6	1.27	1.25	
B7–H7–6	1.28	1.26	
B8–H8–9	1.26	1.26	
B10–H10–9	1.27	1.23	
av	1.26 [1]		1.326 [3]
B6–H5–6	1.28	1.28	
B6–H7–6	1.32	1.44	
B9–H8–9	1.27	1.35	
B9–H10–9	1.29	1.35	
av	1.32 [5]		1.349 [3]

[a] Esd's of individual distances are 0.017–0.023 Å. [b] See ref. 27. The esd's of individual distances are reported as 0.004–0.006 Å. [c] The numbers in square brackets, corresponding to the least significant digits of the adjacent angles, are the root-mean-square deviations from the averages.

to produce an apparent slight shortening of the distances, as is found.

Our B–H distances (Table V) and H–B–H and H–B–B angles (Table VI) compared with those for $B_{10}H_{14}$ seem about as reliable as one would expect in an X-ray analysis. The average terminal B–H bond length is ~0.07 Å shorter than found in the neutron work on $B_{10}H_{14}$. The average B–H distances in both the short and long arms of the B–H–B bridge bonds are shorter than in $B_{10}H_{14}$, though not to the same degree. Since Brill et al.[27] did not do so, it is pertinent here to remark that their corrected refinement of the structure of $B_{10}H_{14}$ reduced the apparent difference between the averaged distances for the short and long B–H bridge arms from 0.053 to 0.023 Å.

The angles of the types B–B–B′ and B–B′–B′ displayed at the top left of Table IV are all very close to the corresponding angles B–B–H in $B_{10}H_{14}$, suggesting that there is little repulsion between nonbonded atoms belonging to two different halves of the molecule. This is consistent with the fact that the closest approach for such atoms, the H10···H′1 distance, is 2.68 Å (uncorrected).

The packing of the molecules is shown in the stereoscopic drawing of Figure 2. There are no unusually close contacts between molecules. The closest contacts for the three kinds of atom pairs are B···B = 3.908 Å, B···H = 3.077 Å, and H···H = 2.38 Å (all uncorrected).

Analysis of Thermal Motion. The thermal-motion ellipsoids of 10% probability[25] shown in Figure 1 appear generally sensible, except for some of the hydrogen-atom ellipsoids, which are not expected to be determined accurately. The principal-axis root-mean-square vibration amplitudes range from 0.184 to 0.302 Å for the boron atoms and from an anomalous 0.069 Å to 0.475 Å for the hydrogen atoms.

In order to obtain the corrections to the interatomic distances and angles which are included in Tables III and IV as explained above, we made a segmented-body analysis of the boron atom thermal parameters by use of the program ORSBA of Johnson.[37] The boron skeletons of the two $B_{10}H_{13}$ groups were treated as two coupled rigid bodies constrained so as to have the same translational motion. The least-squares fit of the segmented-body parameters to the set of observed boron U_{ij} data[38] was good, the root-mean-square deviation between observed and calculated data being 0.0019 Å. The root-mean-square principal-axis librational amplitudes calculated for the unprimed group were 5.9, 1.97, and 1.01° and for the primed group were 5.78, 3.60, and 0.57°. For each group the principal axes of libration lie close to the principal axes of inertia of the whole molecule; the largest root-mean-square amplitude is associated with the smallest moment of inertia and the smallest amplitude with the largest moment. The inertial axis of smallest moment lies almost along the B1-B′5 bond.

Registry No. $B_{20}H_{26}$, 69943-44-8.

Supplementary Material Available: A table of anisotropic thermal parameters for the hydrogen atoms, a table of angles H–B–H and H–B–B, and a table of observed and calculated structure-factor squares, with standard errors of the former (19 pages). Ordering information is given on any current masthead page.

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Properties and Reactivities of Pentadentate Ethylenediaminetetraacetate Complexes of Ruthenium(III) and -(II)

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The reaction of the pentadentate edta complex of ruthenium(III) with various entering ligands L has been studied as a function of pH, temperature, and L at 0.2 M ionic strength in aqueous solution. Over the pH range 0.8–8.5, the species $Ru^{III}(edta)H_2O^-$ is the sole form reactive in the substitution processes. Both forward (k_1) and reverse (k_{-1}) rate constants

$$Ru(edta)H_2O^- + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(edta)L^- + H_2O$$

have been determined, as well as activation parameters for the complexation (k_1) process (L, k_1 in $M^{-1}\ s^{-1}$ (25 °C), k_{-1} in s^{-1} (25 °C), $\Delta H_1^{\ddagger}$ in kcal mol^{-1}, $\Delta S_1^{\ddagger}$ in cal $deg^{-1}\ mol^{-1}$): acetonitrile, 30 ± 7, 3.2 ± 0.2, 8.3 ± 0.5, −24 ± 4; thiocyanate, 270 ± 20, 0.5 ± 0.1, 8.9 ± 0.5, −18 ± 3; pyridine, 6300 ± 500, 0.061 ± 0.002; isonicotinamide, 8300 ± 600, 0.7 ± 0.2, 6.6 ± 0.5, −19 ± 3; pyrazine, 20 000 ± 1000, 2.0 ± 0.5, 5.7 ± 0.5, −20 ± 3. Forward rate constants for the analogous substitution reaction for $Ru^{II}(edta)H_2O^{2-}$ (25 °C, 0.2 M ionic strength) are as follows: thiocyanate, 2.7 ± 0.2 $M^{-1}\ s^{-1}$; acetonitrile, 13 ± 1 $M^{-1}\ s^{-1}$; isonicotinamide, 30 ± 15 $M^{-1}\ s^{-1}$. The substitution reactions of $Ru^{III}(edta)H_2O^-$ proceed by an associative mechanism, while those of $Ru^{II}(edta)H_2O^{2-}$ appear to be dissociative in nature. Spectra and reduction potentials for the $Ru(edta)L^{-/2-}$ complexes are reported.

Introduction

Although ethylenediaminetetraacetate (edta) complexes of Ru(III) have been known for more than a decade,[1-3] knowledge of the chemistry of these systems is quite limited. Electrochemical studies[4] have shown that electron transfer is rapid and reversible for the $Ru(edta)H_2O^{-/2-}$ couple and that $Ru^{II}(edta)H_2O^{2-}$ is oxidized by perchlorate ion. Recently, Shimizu[5] has reported the reaction of $Ru^{II}(edta)H_2O^{2-}$ with formate ion to form the carbonyl complex $Ru^{II}(edta)CO^{2-}$ at an appreciable rate. Oyama and Anson[6] have accomplished the attachment of the edta complex of Ru(III) to a graphite electrode surface through the uncoordinated carboxylate group of edta and reported electrochemical data for several $Ru(edta)L^{-/2-}$ couples.

We have found that it is possible to generate an extensive series of substituted pentadentate edta complexes of both ruthenium(III) and ruthenium(II) ($Ru^{III}(edta)L^-$ and $Ru^{II}(edta)L^{2-}$) in which L ranges from water to N aromatic heterocycles.[7] Analogous series have been characterized for $Ru(NH_3)_5L^{3+}$ and $Ru(NH_3)_5L^{2+}$.[8,9] Comparison of the properties of this edta series with those of the ammines may provide insight concerning the role of the ligands in determining the reactivity and properties of the metal center. Further, since the substituted species Ru(edta)L may be generated for both Ru(III) and Ru(II), the role of the metal oxidation state may be systematically explored for this series as has been done for the ammines.[10-12]

In preliminary studies, we discovered similarities in the properties of $Ru^{II}(edta)L^{2-}$ and $Ru(NH_3)_5L^{2+}$. When L is an aromatic N heterocycle, the visible metal-to-ligand charge-transfer spectra are very similar. Studies of the rates of formation of such complexes revealed, however, that the reactivities of the edta complexes toward substitution differ dramatically from those of $Ru(NH_3)_5H_2O^{3+}$ and $Ru(NH_3)_5H_2O^{2+}$.[9,13-19] In this report we present the results of studies of the substitution reactions of $Ru^{III}(edta)H_2O^-$ and $Ru^{II}(edta)H_2O^{2-}$, as well as spectral and electrochemical properties of the $Ru(edta)L^{-/2-}$ complexes.

Experimental Section

Materials. The pentadentate ethylenediaminetetraacetate (edta) complex of ruthenium(III), $Ru(Hedta)H_2O{\cdot}4H_2O$, was prepared according to the literature procedure.[1] Electronic and infrared spectra of this complex agreed well with the reported values.[1] The complex was also characterized by titration with a standard sodium hydroxide solution in 0.2 M potassium trifluoromethanesulfonate (Ktfms).

The complex anion $Ru^{II}(edta)H_2O^{2-}$ was prepared in situ in acetate buffer solution by the reduction of $Ru^{III}(edta)H_2O^-$ with zinc amalgam under argon or with molecular hydrogen at a platinum-black surface.

Commercial trifluoromethanesulfonic acid (Htfms, 3 M Co.) was purified by distillation under reduced pressure (bp 54 °C (8 torr)). The initial and final 10% aliquots were discarded and the middle 80% fraction was collected. Ktfms was obtained by neutralizing a warm aqueous Htfms solution with potassium carbonate. All other reagents were the highest purity commercially available and were used without further purification. Triply distilled water was used throughout.

Physical Measurements. UV and visible spectral measurements were carried out with Cary 14 and 17 spectrometers. For the binding of $Ru(edta)H_2O^-$ to acetonitrile, equilibrium constants were calculated from slope-to-intercept ratios of plots of $(\Delta A)^{-1}$ vs. $[L]^{-1}$, where ΔA is the absorbance change accompanying complexation and [L] is the molar concentration of the ligand.[20] The electronic spectral band maxima and molar absorptivities of $Ru^{III}(edta)L^-$ and $Ru^{II}(edta)L^{2-}$ were measured for equilibrated solutions in which more than 90% of the Ru species was complexed with a single L. This procedure was necessary since a second molecule of L may coordinate at high concentrations of L.

Rates of rapid reactions were measured with a Durrum-Gibson stopped-flow instrument which was modified as previously described.[21] Slower reaction rates were measured with Cary 14, 16, and 17 spectrometers. The substitution kinetics were studied in the presence of at least tenfold excess ligand. The redox processes were studied

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