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Theoretical Study of the Isomerization of Hypothetical B_4H_4

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The pathway for the degenerate rearrangement of tetrahedral and planar B_4H_4 has been investigated. The tetrahedral T_d structure is the most stable. A structure of symmetry D_{2d} lies in a shallow minimum, separated by a barrier of about 8 kcal/mol on the pathway to the T_d structure. This barrier arises from an orbital crossing phenomenon. Because the planar D_{4h} structure is not in a local minimum, it can be regarded as a transition state between two symmetry-equivalent D_{2d} structures. We find that the effects of electron correlation are important: the tetrahedral structure is predicted to be more stable than the square-planar structure by 32.8 kcal/mol at the 6-31G level and by 74.2 when correlation correction is included. Also, polarization stabilizes the tetrahedral structure more than it stabilizes the planar structure.

Introduction

Interest in the B_4X_4 family has increased since the reported synthesis[1] of tetra-*tert*-butyltetraborane, *t*-Bu_4B_4. The only previously known member, B_4Cl_4, was assumed to be stabilized by back-bonding from the halogen to the boron cage. It now appears that extensive back-bonding is not essential for the formation of a B_4R_4 structure, where R is *tert*-butyl, although the geometry of this new species has not been established. The B_4Cl_4 structure is tetrahedral.[2,3] An earlier theoretical study[4] has predicted that B_4F_4 is about equally stable in tetrahedral and square-planar forms which are separated by a high barrier. The prototype molecule and the simplest for accurate theoretical study is hypothetical B_4H_4, which has been predicted to be tetrahedral.[4] The availability of more advanced theoretical methods had prompted us to restudy the reaction pathway between the planar and tetrahedral forms, especially in the neighborhood of the symmetry crossing of the intermediate D_{2d} symmetry. In particular, we have been able to include geometry optimization within D_{2d} symmetry, as well as study the effects of basis sets and of electron correlation on both assignments of electron occupancy.

In our previous description, the barrier was 9 kcal/mol above the planar form. However, the geometries of all intermediate structures were D_{2d} structures in which the B–H is constrained to be directed away from the center of the B_4 bisphenoid. In the present study, further geometrical optimization has been carried out in which the angle between the BH bond and the boron to molecular center has been optimized, along with optimization of both B–B and B–H distances. The degenerate rearrangement of B_4H_4 from T_d to D_{4h} involves an orbital crossing. The molecular orbital configuration for the valence electrons in the ground state is $(a_{1g})^2(e_u)^4(b_{2g})^2$. As the tetrahedral structure is distorted, the occupied t_2 orbital transforms under D_{2d} symmetry as b_2 and e while the b_{2g} orbital of the D_{4h} structure transforms as b_1. An orbital crossing occurs for the tetrahedral rearrangement when the energy of the b_1:b_2 configuration (LUMO:HOMO) is the same as that of the b_2:b_1 configuration.

Normally reactions involving orbital crossings are considered to have significant activation barriers.[5] As we describe below, the barrier near the symmetry crossing in B_4H_4 is surprisingly small. While the previous calculation gave the symmetry crossing at a higher energy than either the planar or tetrahedral form, our new results show that the crossing is at a lower energy than the planar form, which is now predicted to be unstable with respect to distortion to a marginally stable intermediate of D_{2d} symmetry.

Procedures

All calculations were performed with Gaussian 80 program package.[6] Geometries were optimized at the 3-21G level[7] and single point calculations were made at the 6-31G level plus third-order[8] Møller–Plesset[9] correlation correction (MP3/6-31G) (Table I). A reaction coordinate was taken as the angle made between the center of the molecule and two boron atoms. Points along the reaction path were fully optimized within D_{2d} symmetry with the reaction coordinate fixed at 0.1 path coordinate (PC) intervals between the T_d structure (109.471°) and the D_{4h} structure (180.0°). A crossing was observed at the 6-31G level between PC = 0.3 and PC = 0.4 (Figure 1). The higher energy surface was calculated at two additional points by changing the occupation and reoptimizing at the 3-21G level (Figure 1). Although the shape of the curve is nearly constant when CI is introduced, the b_1:b_2 surface is stabilized relative to the b_2:b_1 surface by approximately 30 kcal/mol and the crossing is delayed to the interval between PC = 0.4 and PC = 0.5 (Figure 2). Polarization at the 6-31G* level stabilizes the T_d structure an additional 12.0 kcal/mol when compared to the 6-31G level (Table II). If the effect is constant for the respective surfaces, the crossing might be further delayed but would probably not affect the crossing barrier significantly. Energies relative to the T_d structure are summarized in Table II.

An earlier study[4] of the B_4H_4 surface using the linear synchronous transit (LST) pathway[10] predicted an orbital crossing at PC = 0.6 and a crossing barrier of 24 kcal/mol using PRDDO[11] and a GVB[12] wave function. The orbital crossing was delayed to PC = 0.8, and a barrier of 9 kcal/mol was predicted with the use of an ab initio wave function plus CI. The LST pathway, the path of least motion connecting the T_d and D_{4h} structures, does not permit intermediate geometry relaxation.

The line crossing located in this paper represents optimal geometries for each surface and thus does not represent an orbital crossing point. An orbital crossing point is the lowest energy which is the same for both configurations *and* for the same geometry. So that an approximate barrier to orbital crossing could be calculated, the geometries of the b_2:b_1 and b_1:b_2 surfaces were linearly interpolated at PC = 0.475. The MP3/6-31G energy was evaluated at both occupations for the average geometry. The calculated energies differed by 3.6

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(1) Davan, T.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 250.
(2) Urry, G.; Wartik, T.; Schlesinger, H. *J. Am. Chem. Soc.* **1952**, *74*, 5809.
(3) (a) Atoji, M.; Lipscomb, W. N. *J. Chem. Phys.* **1953**, *21*, 172. (b) Atoji, M.; Lipscomb, W. N. *Acta Crystallogr.* **1953**, *6*, 547.
(4) Kleier, D. A.; Bicerano, J.; Lipscomb, W. N. *Inorg. Chem.* **1980**, *19*, 216.
(5) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.
(6) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN-80, *QCPE* 406 (Indiana University).
(7) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(8) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem., Quant. Chem. Symp.* **1976**, *No. 10*, 1.
(9) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(10) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.
(11) Halgren, T. A.; Lipscomb, W. N. *J. Chem. Phys.* **1973**, *58* 1569.
(12) Hunt, W. J.; Hay, P. J.; Goddard, W. A. *J. Chem. Phys.* **1972**, *57*, 738.

0020-1669/81/1320-4148$01.25/0

Table I. Summary of Optimized Geometries and Total Energies (hartrees) for B_4H_4

Tetrahedron Surface $b_1:b_2$

PC[a]	0.0	0.2	0.3	0.4	0.5	0.6	0.8	1.0	0.475
central angle[b]	109.471	123.576	130.630	137.682	144.736	151.788	165.894	180.0	142.500
BB dist[c]	1.7104	1.6683	1.6662	1.6730	1.6863				1.6948
BB dist[d]	1.7104	1.8796	1.9757	2.0754	2.1752				2.1607
BH dist	1.1757	1.1758	1.1761	1.1767	1.1779				1.1784
BH angle	180.0	174.081	171.174	168.396	165.980				155.380
6-31G	100.868 660	100.850 460	100.831 806	100.809 962	100.786 558				100.785 777
MP3/6-31G	101.144 759	101.127 969	101.110 036	101.091 081	101.069 886				101.069 264
6-31G*	100.924 777								

Square-Planar Surface $b_2:b_1$

PC[a]	0.2	0.3	0.4	0.5	0.6	0.8	1.0	0.475
central angle[b]	123.576	130.630	137.682	144.736	151.788	165.894	180.0	142.500
BB dist[c]	1.7265	1.7133	1.7076	1.7083	1.7153	1.7358	1.7994	1.6948
BB dist[d]	1.9452	2.0315	2.1183	2.2036	2.2857	2.4432	2.5448	2.1607
BH dist	1.1723	1.1749	1.1775	1.1802	1.1830	1.1876	1.1888	1.1784
BH angle	142.807	142.769	143.291	144.349	146.166	155.199	180.0	155.380
6-31G	100.786 214	100.819 002	100.840 366	100.851 445	100.853 247	100.835 221	100.816 382	100.839 140
MP3/6-31G	101.023 235	101.051 069	101.069 562	101.077 977	101.077 650	101.054 658	101.026 575	101.063 478
6-31G*						100.870 825	100.853 331	

[a] PC = path coordinate. [b] Central angle is the angle two borons make with the center of symmetry in degrees; all distances are in Å. BH angle is the angle formed between BH and the molecular center to boron; all angles are in degrees. [c] Adjacent boron atoms. [d] Nonadjacent boron atoms.

Table II. Relative Energies (kcal/mol) for $b_1:b_2$ (Top) and $b_2:b_1$ (Bottom) Surfaces

PC[a]	0.0	0.2	0.3	0.4	0.5	0.6	0.8	1.0	0.475
6-31G	0	11.42	23.13	36.83	51.52				
MP3/6-31G	0	10.54	21.22	33.68	46.99				
6-31G	0	51.73	31.16	17.75	10.80	9.67	20.98	32.80	18.52
MP3/6-31G	0	76.26	58.43	47.19	41.91	42.11	56.54	74.16	51.00
6-31G*	0						33.85	44.83	

[a] PC = path coordinate.

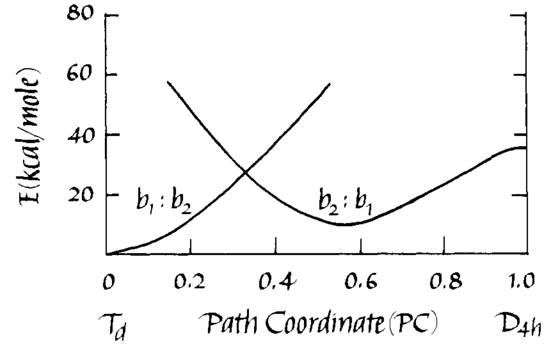

Figure 1. Potential energy curves at the 6–31G level for rearrangement of B_4H_4. Geometries were optimized at the 3–31G level.

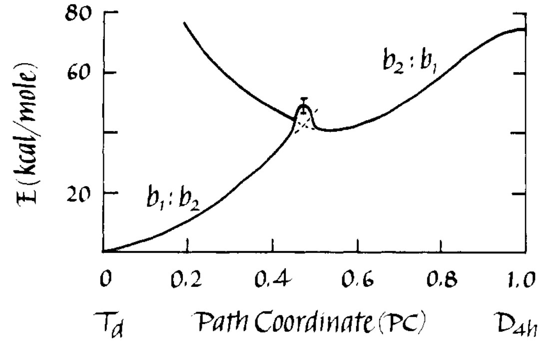

Figure 2. Potential energy curves at the MP 3/6–31G level for rearrangement of B_4H_4. Geometries were optimized at the 3-21G level. The shape in the region of crossing is not well defined.

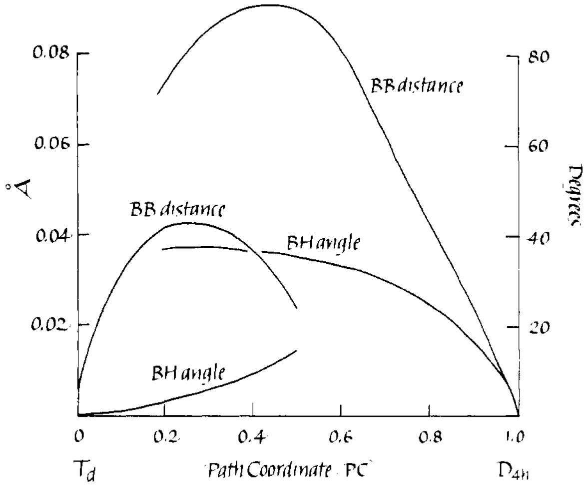

Figure 3. Plot of change in bonded BB distance and centrally defined BH angle vs. path coordinate from T_d and D_{4h} structures.

kcal/mol. The average of these values led to a predicted barrier of about 8 kcal/mol.

Geometries. In an earlier study,[4] a barrier of 9 kcal/mol from the D_{4h} structure was calculated. The barrier of ~8 kcal/mol found here is similar in magnitude but is from a D_{2d} structure, not the D_{4h} structure which is now a transition state. The difference in the two predictions is due almost entirely to geometry relaxation along the reaction path. As the molecule is distorted from D_{4h} symmetry, there is an initial significant movement of the hydrogens out of the molecular plane accompanied by an expansion of the boron ring. The geometries are summarized in Table I.

The rate of change of the B–B distance and the angle formed with BH and the center of symmetry is shown in Figure 3. From PC = 1.0 to PC = 0.5 the change is very rapid on the $b_2:b_1$ surface. There is a minimum in the B–B distance of 1.71 Å while the angle approaches 142.8°. The accompanying changes upon distortion of the T_d structure are less drastic. There is an initial contraction of the four shorter B–B distance to a minimum of 1.67 Å at PC = 0.3. The angle formed between BH and the molecular center to boron is seen to decrease from 180° linearly with respect to reaction co-

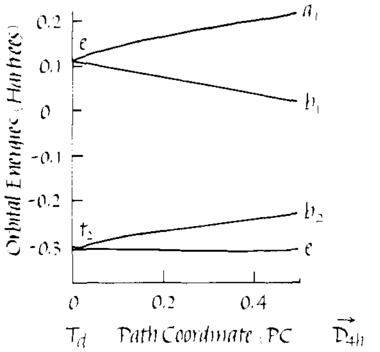

Figure 4. Plot of orbital energies vs. path coordinate for b_1:b_2 surface.

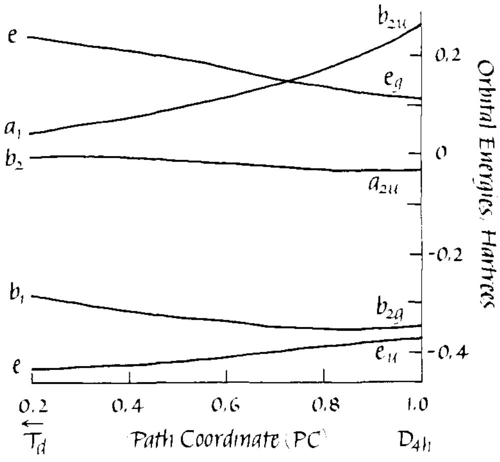

Figure 5. Plot of orbital energies vs. path coordinate for b_2:b_1 surface.

ordinate; because of the compensating effect of the reaction coordinate, the four H atoms tend to remain approximately pointed to the corners of a tetrahedron.

The reason for these changes can be seen from the changes in orbital energy along the reaction path (Figures 4 and 5). The orbital crossing involves the interchange of b_2 and b_1 as the HOMO of the distorted T_d and D_{4h} structure, respectively, in agreement with the KBL study.[4] As the D_{4h} structure is distorted, the b_1 orbital is destabilized, as expected. The minimum in D_{2d} geometry exists due to the stabilization of the e orbital (Figure 6) which favors the bending distortion of B–H bonds. This distortion avoids the unfavorable cross-annular boron p lobe repulsion. There is a tendency for the hydrogen to follow the boron p lobe in order to maintain a bonding overlap. From PC = 0 to PC = 0.6, the stabilization due to the e orbitals exceeds the destabilization due to the b_1 orbital. After this point, however, the destabilization of b_1 becomes dominant.

The e orbitals of the distorted T_d structure are also represented by Figure 6. Here, the hydrogens are already in a favorable position for maximum overlap while avoiding cross-annular repulsion, and the energy of the e orbitals shows no significant variation in energy (Figure 4).

Although the barrier from D_{2d} to T_d of 8 kcal/mol found here for B_4H_4 is comparable with that found earlier from D_{4h} to T_d, there is yet a possibility that further improvement in the wave function may cause this barrier to become smaller or even to disappear.

The potential energy curve for a similar system Be_4 has been reported.[13] The number of cage electrons is identical, and the same b_2:b_1 orbital crossing is observed. Geometries in the study were linearly interpolated and STO-3G energies were evaluated for both occupations. The most notable contrast with B_4H_4 is that the energy along the b_2:b_1 surface increases as Be_4 is distorted from D_{4h}. The reason is that the distorted D_{4h} structure cannot be stabilized by geometry reorganization as is possible for B_4H_4.

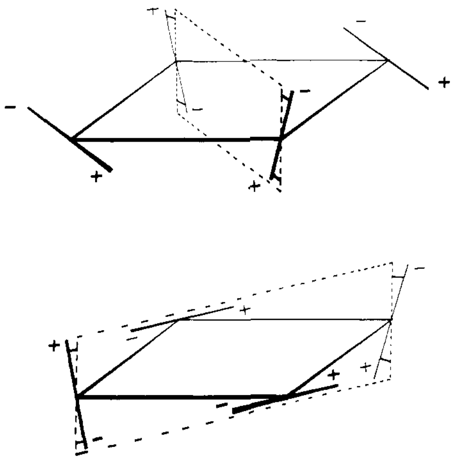

Figure 6. Representation of e-type orbitals for B_4H_4 of D_{2d} symmetry. Two of the p orbitals are titled within the plane constructed of dots. The other two lie approximately in the horizontal plane defined by solid lines. Steric repulsion is greater for larger angles that are indicated by small arcs lying in the dotted plane or its extension.

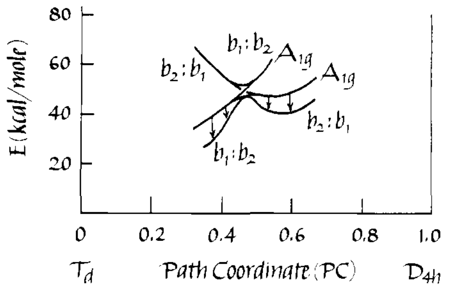

Figure 7. Schematic representation of avoided A_{1g} crossing. The arrows represent a stabilization of the occupied surfaces (the b_1:b_2 surface at the left until the crossing point is reached and then the b_2:b_1 surface) through geometry relaxation.

Tunneling.[14] The crossing of the b_2:b_1 and b_1:b_2 surfaces can be viewed as an avoided orbital crossing within two A_{1g} states. Figure 7 is thus a slice through coordinate space. In reality, geometry relaxation will lower the energy of the occupied surface. However, at the crossing point there is a common geometry. The barrier therefore has as a component the energy needed to distort the optimized geometries to the common geometry of transition.

We believe that it is unlikely that the D_{2d} intermediate can be isolated successfully. The main distortion to the crossing geometry involves motion of the four hydrogens perpendicular to the plane of the D_{4h} structure. If one assumes a parabolic barrier with ν = 800 cm^{-1} (imaginary), then at room temperature the transmission coefficient for a proton tunneling is 2.04.[14a] This value corresponds to an increase by a factor of 2 in the rate of reaction due to tunneling and can be compared to an increase by a factor of 10 in the rate of inversion in ammonia[14b] for which the barrier is 5.7 kcal/mol. In ad-

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(13) Whiteside, R. A.; Krishnan, R.; Pople, J. A.; Krogh-Jespersen, M.-B.; Schleyer, P. v. R. *J. Comput. Chem.* **1980**, *1*, 307.

(14) (a) With use of $\kappa_T = (^1/_2\mu_t)/\sin(^1/_2\mu_t)$ with $\mu_t = h\nu_t/kT$: Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1959; p 209. (b) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: New York, 1980; p 153. (c) A theoretical study of tunneling in formaldehyde: Gray, S. K.; Miller, W. H.; Yamaguchi, Y.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1981**, *103*, 1900. (d) A theoretical study of tunneling in vinylidene: Osamura, Y., Schaefer, H. F. III; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904.

Table III. Relative Energies (kcal/mol) of B_4X_4 Structures

$T_d - D_{4h}$	STO-3G	STO-3G*	MP2/ STO-3G	KBL[b]
B_4H_4	37.9			38.8[c]
B_4F_4	9.8			10.0[d]
Me_4B_4[a]	38.3			
B_4Cl_4	−18.2	−19.0	35.0	

[a] Methyl groups prevent exact symmetry of D_{4h}. [b] Reference 4. [c] STO-3G basis. [d] Double ζ.

dition to this effect, the zero-point energies of the D_{2d} intermediate and the crossing point geometry will also reduce the calculated barrier because at the crossing point one mode becomes imaginary and does not contribute.

Although B_4F_4 and Me_4B_4 are too large to be studied at the same level of theory as that used here for B_4H_4 (~40 h on a VAX 11/780 computer), we find that STO-3G calculations predict T_d ground states for both B_4F_4 and Me_4B_4. The calculations were made using the boron coordinates optimized in B_4H_4 and bond lengths for carbon (1.57 Å) and fluorine (1.293 Å) taken from STO-3G-optimized[15] bond lengths in BH_2CH_3 and BH_2F. The calculated relative energies for B_4H_4 and B_4F_4 compare well with minimal basis set calculations of KBL (Table III). The T_d structure of Me_4B_4 is predicted to be 38.3 kcal/mol more stable than the structure which has coplanar B and C atoms. This last structure has D_{2d} symmetry rather than D_{4h} symmetry because of the hydrogen atoms. Distortions of the methyl groups similar to those seen experimentally[16] for the *tert*-butyl groups in *t*-Bu_4C_4 are expected to be small or negligible. However, CI corrections should favor the T_d structure.

Our STO-3G energies for B_4Cl_4 indicate[17] that the planar structure is more stable, in contradiction to experiment. However, this basis set is known to be inadequate[18] for third-period elements. Polarization (STO-3G*) does not affect the predicted relative stabilities of the structures (Table III). Correlation correction at the MP2/STO-3G level, however, is sufficient to reverse these stabilities. The T_d structure is now predicted to be 35.0 kcal/mol more stable than the D_{4h} structure. It is known[19] that B_4Cl_4 is nonfluctional over a 200 °C temperature range.

The recent experimental synthesis of *t*-Bu_4B_4[1] and B_9I_9[20] have shown that back-bonding from halogen to the boron cage does not rationalize the violation of the often useful framework electron count-structural correlation (Wade's rules).[21] This effect is almost absent in *t*-Bu_4B_4 and weak for B_9I_9.

Conclusion

The rearrangement of T_d–D_{4h}–T_d is predicted to occur with an orbital crossing but *not* as the rate-limiting step. A D_{2d} intermediate is formed with an approximate 8 kcal/mol barrier to the T_d structure. The D_{4d} structure is a transition state 34 kcal/mol higher than the D_{2d} minimum to an equivalent D_{2d} minimum which then rearranges to its equivalent T_d structure. The angle formed with BH and the center of symmetry is 180° for both the D_{4h} and T_d structures but departs significantly in the reduced symmetry of D_{2d}. The effect of relaxing this earlier constraint has made a major change in prediction.

Although the calculations do not predict the energetics of other competing reactions, B_4H_4 (if made) should be tetrahedral and not fluctional. Back-bonding in B_4F_4 favors the planar structure, and the best estimate by KBL predicts the two forms of B_4F_4 to be about isoenergetic. On the other hand, B_4Cl_4 is calculated as most stable in the tetrahedral geometry if electron correlation corrections are included.

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---

(15) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3402.

(16) Irngartinger, H.; Riegler, N.; Malsch, K.-D.; Schneider, K.-A.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 211.

(17) A B–Cl distance of 1.69 Å was used (ref 3b).

(18) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(19) Davan, T.; Morrison, J. A. *Inorg. Chem.* **1979**, *18*, 3194.

(20) Wong, E. H. *Inorg. Chem.* **1981**, *20*, 1300.

(21) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446.

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Hydrolytic Polymerization of Chromium(III). 2. A Trimeric Species

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With use of an ion-exchange displacement elution, a green species was separated from mixtures of Cr(III) polymers and its absorption spectrum determined. The hydroxides per chromium atom were found to be $^4/_3$, and the charge per chromium atom was shown to be consistent with this value. The degree of polymerization from freezing point depression was close to 3. Measurements are reported for the equilibrium quotient for the formation of the trimer from the monomer. The ESR spectrum and magnetic susceptibility were determined, and the results are discussed in terms of possible structures.

Laswick and Plane[2] reported the isolation of a green polymeric species from refluxed solutions of chromium(III) perchlorate by ion-exchange techniques, using a 0.2 M solution of $La(ClO_4)_3$ as eluant. Their investigation showed the green species to be a more highly polymerized form than a second species, later identified as a dimer,[3-5] also isolated from the same refluxed solutions. Their conclusion was based upon the observed elution behavior: the green species is more tightly held than the dimeric species and is far more sensitive to eluant

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(1) Name changed from Gertrude Thompson.

(2) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

(3) M. Ardon and A. Linenberg, *J. Phys. Chem.*, **65**, 1443 (1961).

(4) R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

(5) M. E. Thompson and R. E. Connick, *Inorg. Chem.*, **20**, 2279 (1981); hereafter referred to as paper 1.