Kinetics and mechanism of complex formation between (oxalatopentaamminecobalt(III) and iron(III) in acidic aqueous solution

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Kinetics and Mechanism of Complex Formation between (Oxalato)pentaamminecobalt(III) and Iron(III) in Acidic Aqueous Solution

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Previous studies by one of us have dealt with the kinetics of Fe(III)-catalyzed hydrolysis of (oxalato)(amine)cobalt(III) complexes ($N_5CoC_2O_4^+$, $N_5 = (NH_3)_5$, $(en)_2(NH_3)$).[2,3] The kinetic data could be interpreted in terms of the rapid and reversible equilibrium preassociation of Fe(III) with the $N_5CoC_2O_4^+$ species to form the precursor complex, $N_5CoC_2O_4Fe^{4+}$, followed by the catalyzed water substitution at the cobalt(III) center to yield $N_5CoOH_2^{3+}$ and mono(oxalato)iron(III) species. The solution equilibria involving the formation of the binuclear species of Fe(III) and several other di- and trivalent nonreducing substitution-labile metal ions with $(NH_3)_5CoC_2O_4^+$ have also been investigated spectrophotometrically.[4] Data on the kinetics of the very rapid formation of such binuclear species are at present not available, though studies have been made of the formation kinetics of many mononuclear Fe(III) complexes.[5,6] A later paper in the present series will deal with the analogous reaction between Fe(III) and (salicylato)pentaamminecobalt(III) cations of the type $N_5CoOCOC_6H_4OH^{2+}$, where $N_5 = (NH_3)_5$, $(en)_2(NH_3)$, and tetraethylenepentamine, providing further insight into the nature of these very rapid binuclear complexations.

Experimental Section

Materials and Method. (Oxalato)pentaamminecobalt(III) perchlorate, $[(NH_3)_5CoC_2O_4H](ClO_4)_2$, was prepared by the standard procedure.[7] λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$): 507 (74.0) for $(NH_3)_5CoC_2O_4H^{2+}$ in 0.1 M $HClO_4$ medium, which agrees well with the previously reported values.[8] Iron(III) and the free acid content of the stock solution of iron(III) perchlorate (G. F. Smith Chemical Co.) were estimated by EDTA titration and pH measurement, respectively. Fisher Certified reagents were used. The ionic strength of the reaction mixture was adjusted with sodium perchlorate. Solutions were prepared in laboratory distilled water, which was further purified by passage through a mixed-bed ion-exchange column. A Cary 118C UV-visible spectrophotometer was used for spectral measurements.

Rate Measurements. The kinetics of complexation of $(NH_3)_5CoC_2O_4H^{2+}$ with Fe(III) was investigated at $20.0 \le t \le 30.0$ °C and $I = 1.0$ M. The rate measurements were made at 350 nm (absorbance increases with time) on an automated Durrum Model 110 stopped-flow assembly. One of the syringes of the apparatus contained the solution of iron(III) perchlorate, whereas the other had the solution of the cobalt(III) complex; both solutions were adjusted to $I = 1.0$ M and the same preselected acidity. Runs were made under pseudo-first-order conditions in the usual way with $[complex]_T = (5.0–8.0) \times 10^{-4}$ M. The observed pseudo-first-order rate constants were calculated by use of a linear least-squares program and are reported as the mean of at least five kinetic runs.

Results and Discussion

Table I presents the observed pseudo-first-order rate constants as a function of total Fe^{3+} concentration, $[Fe^{3+}]_T$, and $[H^+]$ at $20 \le t \le 30$ °C. One notes (see Figure 1 for illustrative data at 25 °C) that the k_{obsd} values increase linearly with $[Fe^{3+}]_T$ at a fixed acidity, that there is a nonzero intercept, that the intercepts are essentially independent of acidity, and that the slopes of the straight lines decrease with increasing acidity. A proposed mechanism for the reaction is presented in Scheme I, where it is assumed that, in the experimental acidity range, all possible reactant species are involved, viz.: $Fe(H_2O)_6^{3+}$ ($\equiv Fe^{3+}$), $Fe(H_2O)_5OH^{2+}$ ($\equiv FeOH^{2+}$), $Co(NH_3)_5C_2O_4^+$ ($\equiv RC_2O_4^+$), and $Co(NH_3)_5C_2O_4H^{2+}$ ($\equiv RC_2O_4H^{2+}$). The corresponding rate law is of the form

$$k_{obsd} = k_f f_1 f_2 [Fe^{3+}]_T + k_r f_3 \quad (1)$$

where

$$k_f = (k_1K_1 + k_4K_h)/[H^+] + k_2 + k_3K_1K_h/[H^+]^2 \quad (2)$$

$$k_r = (k_{-1} + k_{-4}) + k_{-2}[H^+] + k_{-3}K'_h/[H^+] \quad (3)$$

$$f_1 = [H^+]/([H^+] + K_h) \quad (4)$$

$$f_2 = [H^+]/([H^+] + K_1) \quad (5)$$

$$f_3 = [H^+]/([H^+] + K'_h) \quad (6)$$

The known values[9] of 10^3K_h at $I = 1.0$ M are 1.20, 1.64, and 2.29 M at 20, 25, and 30°C, respectively.[10] Also, 10^3K_1 has the values[11] 8.0, 8.8, and 9.5 M at $I = 1.0$ M and the three indicated temperatures, respectively. Values for K'_h are not known, nor can they be derived from our rate data, but can

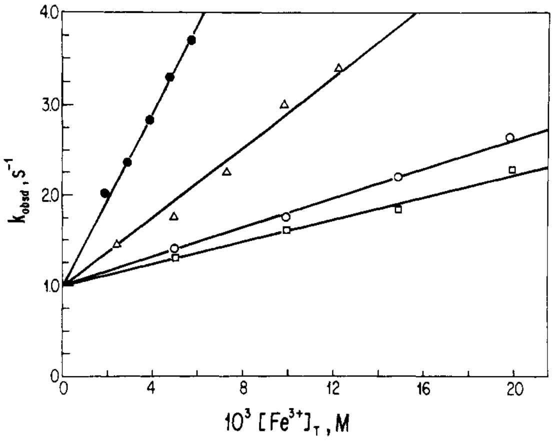
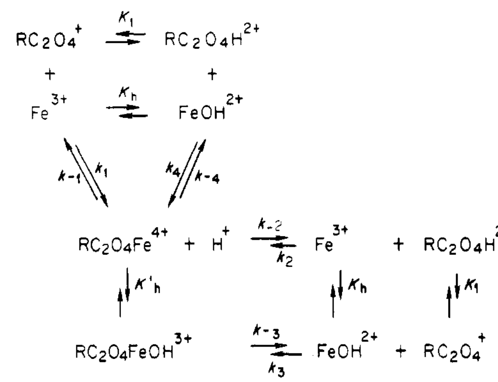


Figure 1. Plot of k_{obsd} vs. $[Fe^{3+}]_T$ at 25 °C. $[H^+]$: ●, 0.05 M; △, 0.1 M; ○, 0.2 M; □, 0.3 M.

Scheme I[a]



[a] Proton dissociations occur in the direction of the arrows adjacent to each dissociation constant.

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(10) With use of these values it can readily be shown that the acidity of the reaction medium as adjusted by added $HClO_4$ is changed only negligibly by the hydrolysis of $Fe(H_2O)_6^{3+}$.
(11) See Table I of ref 2.

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Table I. Rate Data for the Complexation of Aqueous Fe(III) with $(NH_3)_5CoC_2O_4^{+}$ [a]

$10^3 \times [Fe^{3+}]_T$, M	$[HClO_4]$, M	k_{obsd}, s^{-1}	k_r, s^{-1}	k_f, M^{-1} s^{-1}
		20.0 ± 0.1 °C		
2.4	0.1	0.98 ± 0.02	0.79 ± 0.02	78.5 ± 2.5
5.0	0.1	1.18 ± 0.02		
7.4	0.1	1.35 ± 0.02		
10.0	0.1	1.54 ± 0.02		
12.4	0.1	1.77 ± 0.05		
5.0	0.2	0.93 ± 0.02	0.73 ± 0.03	35.0 ± 2.5
10.0	0.2	1.06 ± 0.01		
15.0	0.2	1.24 ± 0.02		
20.0	0.2	1.45 ± 0.01		
5.0	0.3	0.84 ± 0.01	0.73 ± 0.01	22.5 ± 1.0
10.0	0.3	0.95 ± 0.03		
15.0	0.3	1.08 ± 0.02		
20.0	0.3	1.17 ± 0.06		
		25.0 ± 0.1 °C		
2.0	0.05	2.02 ± 0.03	1.14 ± 0.03	439.7 ± 7.7
3.0	0.05	2.39 ± 0.14		
4.0	0.05	2.84 ± 0.14		
5.0	0.05	3.28 ± 0.14		
6.0	0.05	3.70 ± 0.10		
2.4	0.1	1.45 ± 0.01	0.86 ± 0.12	207.9 ± 14.3
5.0	0.1	1.77 ± 0.06		
7.4	0.1	2.30 ± 0.12		
10.0	0.1	3.00 ± 0.17		
12.4	0.1	3.39 ± 0.03		
5.0	0.2	1.39 ± 0.11	0.95 ± 0.04	83.9 ± 3.0
10.0	0.2	1.75 ± 0.04		
15.0	0.2	2.18 ± 0.03		
20.0	0.2	2.63 ± 0.13		
5.0	0.3	1.33 ± 0.05	1.00 ± 0.07	61.0 ± 5.1
10.0	0.3	1.61 ± 0.07		
15.0	0.3	1.85 ± 0.06		
20.0	0.3	2.26 ± 0.05		
		30.0 ± 0.1 °C		
2.0	0.05	3.00 ± 0.06	1.5 ± 0.1	778.1 ± 32.4
3.0	0.05	3.80 ± 0.04		
4.0	0.05	4.49 ± 0.06		
2.4	0.1	2.10 ± 0.05	1.4 ± 0.1	320.7 ± 13.7
5.0	0.1	3.05 ± 0.05		
7.4	0.1	3.75 ± 0.07		
10.0	0.1	4.50 ± 0.10		
5.0	0.2	1.80 ± 0.05	1.17 ± 0.03	133.0 ± 6.0
10.0	0.2	2.50 ± 0.05		
15.0	0.2	3.20 ± 0.05		
20.0	0.2	3.75 ± 0.05		

[a] $I = 1.0$ M; $[Co(III)]_T = (5.6–8.4) \times 10^{-4}$ M.

be assumed[12] to be somewhat smaller than K_h. It follows, therefore that f_1, f_2, and f_3 reduce to unity in the acidity range of the experiments so that eq 1 reduces to

$$k_{obsd} = k_f[Fe^{3+}]_T + k_r$$

Thus, the plots of k_{obsd} vs. $[Fe^{3+}]_T$ (such as Figure 1) yield values of k_f and k_r from the slopes and intercepts, respectively, as recorded in Table I. Referring now to the k_f values, we find that plots of k_f vs. $[H^+]^{-1}$ are nonlinear, but good linear plots

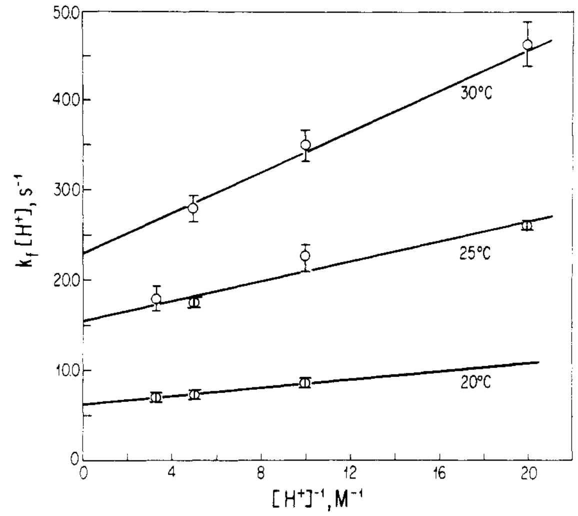

Figure 2. Plot of $k_f[H^+]$ vs. $1/[H^+]$ at various temperatures.

are obtained when $k_f[H^+]$ is plotted vs. $[H^+]^{-1}$ (see Figure 2). This indicates that the k_2 term makes only a minor contribution and is consistent with the recent finding[13] that the analogous rate constant is negligible in the formation of FeA^{2+} when HA is a moderately strong acid such as mono-, di-, or trichloroacetic acid, as is our species $RC_2O_4H^{2+}$. The linear plots for $k_f[H^+]$ vs. $[H^+]^{-1}$ therefore yield values for $(k_1K_1 + k_4K_4)$ from the intercepts and $k_3K_1K_h$ from the slopes, resulting in the data given in the first two columns of Table II. Estimates of k_1 and k_4 may be made as follows. As is discussed later, it may be reasonably assumed that $k_{-1} \cong k_{-4}$, and the cyclic nature of several of the equilibria in Scheme I requires that $k_1K_1/k_4K_h = k_{-1}/k_{-4}$ so that $k_1K_1 \cong k_4K_h$. This enables separate estimates of k_1 and k_4 as given in columns 4 and 5 of Table II. One notes that while $k_1 < k_4 < k_3$, the differences are not great, considering the substantial changes in the nature of the reacting ions. Also, these values are of the same order of magnitude as analogous rate constants for other carboxylate ligands.[5,14,15] Similarly, the rate constants for addition of free oxalate to Fe^{3+} and $FeOH^{2+}$ have been reported[16] as 7.0×10^2, 2.0×10^4, and 8.3×10^3 M^{-1} s^{-1}, respectively, at 25 °C, very close to the values of our analogous constants k_1, k_3, and k_4. This lack of sensitivity to the magnitude and sign of the charges on the reactant ions clearly eliminates the simple S_N2 mechanism concept and supports an I mechanism, as expected for aqueous Fe(III) substitution reactions. There exists considerable controversy as to whether the interchanges are dissociative or associative. Recent determinations of the water-exchange rates[6] of $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ and of the pressure effects on such rates[17] support the assumption of an I_a mechanism for aquo ion substitutions and I_d for the hydroxo congener. Values for the outer-sphere association constant, K_{os}, can only be surmised in our system, but with ion pairs of the types (3+)(1+), (2+)(1+), and (2+)(2+), respectively, for the three reactions, K_{os} cannot be greater than unity.[18] Our values for k_1, k_3, and k_4 at 25 °C thus translate into first-order rates of substitutive water elimination by

(12) The loss of a proton by the species $Co(NH_3)_5C_2O_4Fe(OH_2)_5$ (or $Co(NH_3)_5C_2O_4Fe(OH_2)_4$, if the Fe^{3+} is chelated) will definitely be less facile than by $Fe(H_2O)_6^{3+}$, due to the influence of the negative $C_2O_4^{2-}$ center, as is evidenced by the well-known decrease in acidity of multiply coordinated aquo ions as the number of water ligands is replaced by negative OH^- ligands. An example is the increase in the pK from 4.0 for $Cr(H_2O)_6^{3+}$ to 5.6 for $Cr(H_2O)_5OH^{2+}$, at 25 °C (see footnote 18 of the paper by: Krishnamoorthy, C. R.; Harris, G. M. *J. Coord. Chem.* **1980**, *10*, 65).

(13) Perlmutter-Hayman, B.; Tapuhi, E. *J. Coord. Chem.* **1976**, *6*, 31.
(14) Reference 13, Table III.
(15) Mentasi, E.; Baiocchi, C. *J. Coord. Chem.* **1980**, *10*, 229.
(16) These rate constants, quoted in Table III of ref 13, were calculated from the data of: Moorhead, E. G.; Sutin, N. *Inorg. Chem.* **1966**, *5*, 1866.
(17) Swaddle, T. W., paper presented at Conference on Inorganic Reaction Mechanisms, Wayne State University, Detroit, Mich., June 10–12, 1981.
(18) Simple electrostatic theory predicts a value of about unity for the association of an ion with an uncharged molecule and steadily decreasing values for the association of like-charged ions as the Z_1Z_2 factor becomes more positive. See discussion given by: Hammes, G. G.; Steinfeld, J. I. *J. Am. Chem. Soc.* **1962**, *84*, 4639.

Table II. Kinetic Parameters for the Formation and Dissociation of $(NH_3)_5CoC_2O_4Fe^{4+}$

temp, °C	$(k_1K_1 + k_4K_h)$,[a] s^{-1}	$10^{-4}k_3$,[b] $M^{-1}\ s^{-1}$	$10^{-2}k_1$,[c] $M^{-1}\ s^{-1}$	$10^{-3}k_4$,[c] $M^{-1}\ s^{-1}$	$(k_{-1} + k_{-4})$,[d] s^{-1}
20.0	6.15 ± 0.01	2.3 ± 0.1	3.8	2.5	0.75 ± 0.03
25.0	15.3 ± 1.0	3.7 ± 0.4	8.7	4.6	1.0 ± 0.1
30.0	22.1 ± 1.0	5.4 ± 0.4	11.0	4.8	1.4 ± 0.2
$\Delta H^{\ddagger}$, kcal mol^{-1}		14.5 ± 0.7			10.4 ± 0.6
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}		11.0 ± 2.4			−23.5 ± 2.0

[a] As determined from the intercept values of the plots given in Figure 2. [b] Calculated from the slope values of Figure 2 and the known values of K_1 and K_h at the three temperatures. [c] Calculated by assuming $k_1K_1 = k_4K_h$ (see text). [d] Values of $(k_{-1} + k_{-4})$ are averages of the values of the intercepts of k_{obsd} vs. $[Fe^{3+}]_T$ plots of the type given in Figure 1.

$RC_2O_4^+$ from the $Fe(H_2O)_6^{3+}$ species of $\sim 9 \times 10^2\ s^{-1}$ and from the $Fe(H_2O)_5OH^{2+}$ species by $RC_2O_4^+$ and $RC_2O_4H^{2+}$ of $\sim 4 \times 10^4$ and $\sim 5 \times 10^3\ s^{-1}$, respectively. The water-exchange rate constants for $Fe(H_2O)_6^{3+}$ and $Fe(H_2O)_5OH^{2+}$ are known to be close to 1.6×10^2 and $1.4 \times 10^5\ s^{-1}$, respectively.[6,19] Comparisons of these values with the substitutive rate constants lead to the assignment of the I_a mechanism to our $Fe(H_2O)_6^{3+}$ complexation reaction and of I_d to the two $Fe(H_2O)_5OH^{2+}$ complexations, in total agreement with the conclusions already quoted.[6,17] We were able to determine reasonably precise activation parameters only for the k_3 pathway (see Table II) and these are not substantially different from figures[20] for the reactions of $FeOH^{2+}$ with large anions such as Cl^- and SO_4^{2-}.

It has already been noted that the rate constant for the hydrolysis of the binuclear product complex, k_r, is essentially independent of acidity at each temperature (see Table I and Figure 1). From the form of eq 3, it is obvious that neither k_{-2} nor k_{-3} can contribute perceptibly to the dissociation rate of the complex, so that eq 3 reduces to $k_r = (k_{-1} + k_{-4})$. Furthermore, it is seen that k_{-1} and k_{-4} should be very similar in magnitude, since the transition states for the two reactions must not differ greatly if at all. In fact, any differences in distribution of the hydrolysis products can be expected to be determined at a given acidity of the medium by the very rapid proton transfers governed by K_h and K_1. Experimental confirmation of such an identity is provided by calculations based on the published data[13] concerning the reactions of mono-, di-, and the trichloroacetate species with a aqueous Fe(III), which, as noted above, behave in a manner somewhat similar to our system. Use of these data[21] results in rough estimates at 25 °C for k_{-1} of 12, 17, and 69 s^{-1} and for k_{-4} of 43, 25, and 15 s^{-1}, respectively, for the three chloroacetate species, satisfactorily supporting our conclusion that $k_{-1} \cong k_{-4}$. Our complex $Co(NH_3)_5C_2O_4H^{2+}$ has a pK close to that of CH_2ClCO_2H, but our binuclear product $Co(NH_3)_5C_2O_4Fe^{4+}$ has a charge 2 units greater than $CH_2ClCO_2Fe^{2+}$. The rather slow dissociation rate of the binuclear complex ($k_{-1} \cong k_{-4} \cong 0.5\ s^{-1}$ as compared to $k_{-1} \cong k_{-4} \cong 20\ s^{-1}$ for the acetato species) may be taken as evidence that Fe(III) in the binuclear species is chelated by the oxalate moiety. Similar conclusions were reached from consideration of the stability constants of various analogous binuclear complexes[4] and the high catalytic power of Fe^{3+} relative to H^+ in promoting water-for-oxalate substitution at a cobalt(III) center.[2] The activation parameters for $RC_2O_4Fe^{4+}$ dissociation are quite "normal", being similar to those[20] for a series of FeL^{n+} dissociations, with ΔH^* typically in the range 9–15 kcal mol^{-1} and ΔS^* in the range −10 to −30 cal deg^{-1} mol^{-1}. All in all, one can conclude that $Co(NH_3)_5C_2O_4H^{2+}$ behaves as a conventional ligand in both its association and dissociation reactions involving aqueous Fe(III) species.

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Registry No. $(NH_3)_5CoC_2O_4^+$, 18443-73-7; $Fe(H_2O)_6^{3+}$, 15377-81-8.

(19) Another recent measurement of the water-exchange rate of $Fe(H_2O)_6^{3+}$ ion has yielded a value of 167 s^{-1} at 25 °C (Dodgen, H. W.; Liu, Gordon; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 1002).
(20) Cavasino, F. P. *J. Phys. Chem.* **1968**, *72*, 1378.
(21) Data for k_1, k_4, K_1, K_{HA}, and K_{OH} given in ref 13 and the equality $K_4 = K_1K_{HA}/K_{OH}$ were utilized in this calculation.

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Reaction of Pentaborane(11) with Bis(trimethylphosphine)–Diborane(4)

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Recently we reported[2] that both diborane(6) and tetraborane(10) react with bis(trimethylphosphine)–diborane(4) to give a novel triboron complex cation $B_3H_6[P(CH_3)_3]_2^+$:

$$^3/_2B_2H_6 + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_3H_6[P(CH_3)_3]_2^+B_2H_7^-$$

$$B_4H_{10} + B_2H_4{\cdot}2P(CH_3)_3 \rightarrow B_3H_6[P(CH_3)_3]_2^+B_3H_8^- \quad (1)$$

In these reactions, B_2H_6 and B_4H_{10} are cleaved unsymmetrically: $B_2H_6 \rightarrow$ "$BH_2^+ + BH_4^-$" and $B_4H_{10} \rightarrow$ "$BH_2^+ + B_3H_8^-$". The BH_2^+ unit combines with the diborane(4) adduct to give the triboron cation. The BH_4^- anion further reacts with diborane(6) to form the $B_2H_7^-$ anion.

It was of interest to see if the next higher borane, pentaborane(11), would react with $B_2H_4{\cdot}2P(CH_3)_3$ in the manner similar to that observed for diborane(6) and tetraborane(10). The study of the reaction, which is reported in this paper, showed that the reaction pattern of B_5H_{11} was different from that of B_2H_6 or B_4H_{10}; the unsymmetrical cleavage of B_5H_{11} was not effected by $B_2H_4{\cdot}2P(CH_3)_3$.

Results and Discussion

A rapid reaction occurred at −80 °C between B_5H_{11} and $B_2H_4{\cdot}2P(CH_3)_3$ in a 1:1 molar ratio in dichloromethane to give trimethylphosphine–borane(3) and other compounds. As the reaction solution was allowed to warm, the latter products underwent gradual changes. At room temperature the solution contained $(CH_3)_3PBH_3$, $(CH_3)_3PB_5H_9$, B_5H_9, and B_2H_6 as the final reaction products.

As noted earlier, $B_2H_4{\cdot}2P(CH_3)_3$ cleaved both the B_2H_6 and B_4H_{10} molecules unsymmetrically to give the $B_3H_6[P(CH_3)_3]_2^+$ cation and the anion characteristic of unsymmetrical cleavage of that borane.[2] Since it had been known that B_5H_{11}, like B_2H_6[3] and B_4H_{10},[4] undergoes unsymmetrical cleavage with

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