III. We consider the agreement between the experimental and theoretical values to be remarkably satisfactory in view of the simplicity of the reaction scheme and the cumulative experimental uncertainties. Rather large concentrations of cerium(III) were used both to trap the $SO_4^-\cdot$ radicals efficiently and to minimize the cerium(IV)-$HSO_5^-$ reaction.[1a] In agreement with other studies, we find no reason for invoking a $HSO_5^-$-$SO_4^-\cdot$ reaction.[6c,7]

The stoichiometry of the $HSO_5^-$-$Cr^{2+}$ reaction was briefly examined in view of published observations on the $S_2O_8^{2-}$-$Cr^{2+}$ reaction, for which the mechanism (11)-(14) was proposed.[18]

$$S_2O_8^{2-} + Cr^{2+} = CrSO_4^+ + SO_4^-\cdot \qquad (11)$$

$$SO_4^-\cdot + Cr^{2+} = Cr^{3+} + SO_4^{2-} \qquad (12)$$

$$SO_4^-\cdot + Br^- = SO_4^{2-} + Br\cdot \text{ (or } Br_2^-\cdot) \qquad (13)$$

$$Cr^{2+} + Br\cdot \text{ (or } Br_2^-\cdot) = CrBr^{2+} \qquad (14)$$

Our results are not as clean as those obtained by Pennington and Haim, due primarily to the formation of some polymeric chromium(III) product. However, the data in Table IV are consistent at least qualitatively with an analogous scheme for $HSO_5^-$, with the important difference that $SO_4^-\cdot$ *is not* transferred in the first step. Whether HO· is instead transferred is not known but is a distinct possibility. In principle, an oxygen-18 tracer experiment should settle the issue, but the lack of a suitable precipitant for $Cr^{3+}$ has frustrated our efforts.[19]

The results obtained in this study lead us to suggest that involvement of the sulfate radical anion may be a general feature of the reduction of peroxomonosulfate by 1-equiv reductants. Suitable trapping agents are more limited than in the corresponding peroxodisulfate systems, due primarily to the greater reactivity of peroxomonosulfate toward the immediate product formed when the sulfate radical is scavenged by commonly used species such as vinyl monomers or arsenic(III). Sharply reduced yields of vanadium(V) and complicated kinetic profiles were observed when the latter scavengers were used in the present system.

The kinetic results for the $HSO_5^-$-$VO^{2+}$ reaction are remarkably straightforward in view of the radical mechanism proposed. In contrast, related reductions of hydrogen peroxide by $VO^{2+}$ or $Fe^{2+}$, for example, can exhibit very complicated kinetic and stoichiometric behavior.[20] The principal difference appears to be that the sulfate radical produced as a result of the rate-determining step of the $HSO_5^-$-$VO^{2+}$ reaction primarily oxidizes $VO^{2+}$. In the hydrogen peroxide reactions, the HO· formed in the primary reaction can alternatively oxidize $H_2O_2$ (or $VO_3^+$) to varying extents depending on the experimental conditions, leading to complicated chain reactions. These features are not unexpected in view of the rate constants for reactions 15[20c] and 16[6c] and the rapid oxidation

$$HO\cdot + H_2O_2 = H_2O + HO_2\cdot \quad k = (1.2\text{-}4.5) \times 10^7 \qquad (15)$$

$$SO_4^-\cdot + HSO_5^- = SO_4^{2-} + HSO_5\cdot \text{ (or } SO_5^-\cdot) \quad k < 10^5 \qquad (16)$$

of many substrates by $SO_4^-\cdot$. As suggested previously, the $HSO_5^-$-$HSO_5\cdot$ transformation in peroxomonosulfate reactions may be far less common than the $H_2O_2$-$HO_2\cdot$ involvement in hydrogen peroxide chemistry.[7]

**Registry No.** $HSO_5^-$, 12188-01-1; $VO^{2+}$, 20644-97-7; $Ce^{3+}$, 18923-26-7; $Cr^{2+}$, 22541-79-3.

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# $^{91}$Zr NMR Spectrum of $Zr(BH_4)_4$: The Zr-H Coupling Constant as a Probe for a Fast Intramolecular Process

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$^1$H, $^{11}$B, and $^{91}$Zr NMR spectra have been recorded for the molecule $Zr(BH_4)_4$. The $^{11}$B-decoupled $^{91}$Zr spectrum exhibits a 17-line spectrum with $J_{obsd}$ = 28 Hz; $J_{^{91}Zr-^{11}B}$ was measured as 18 Hz. These data are interpreted in terms of a rapid intramolecular exchange of bridging and terminal hydrogens.

In continuation of our studies[1] on zirconium NMR spectroscopy ($^{91}$Zr is 11.23% abundant; $I = {}^5/_2$; $Q = -0.21 \times 10^{-28}$ m$^2$),[2] we chose to investigate the molecule $Zr(BH_4)_4$ in which the Zr atom is at the center of a tetrahedron of borohydride groups.[3] The initial $^1$H NMR studies[4] showed a 1:1:1:1 quartet due to coupling to a $^{11}$B nucleus ($I = {}^3/_2$) in an effectively tetrahedral environment brought about by a rapid exchange of the single terminal and three bridging protons. On cooling, the $^1$H spectrum exhibited a broadening of the quartet lines; this was originally attributed to a slowing of the bridging H-terminal H exchange process[4] but was later shown to be more consistent with quadrupole broadening concomitant with rapid relaxation.[5]

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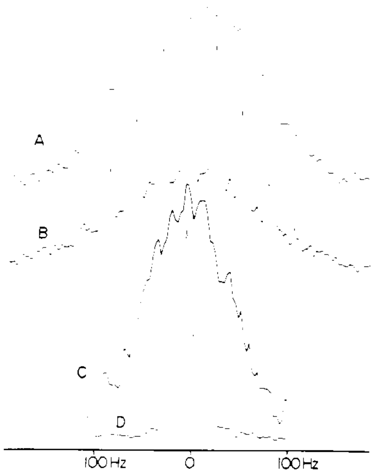

**Figure 1.** $^{91}$Zr NMR spectrum of $Zr(BH_4)_4$ at 25 °C: A, fully coupled; B, $^{11}$B decoupled; C, H decoupled; D, $^{1}$H and $^{11}$B decoupled.

**Figure 2.** Simulated $^{91}$Zr NMR spectrum of $Zr(BH_4)_4$: A, coupled to protons; B, coupled to $^{11}B_4$ and to $^{10}B^{11}B_3$.

The $^{91}$Zr spectrum of $Zr(BH_4)_4$ (Figure 1A) appears as a broad line of half-width 184 ± 10 Hz which, upon $^{11}$B decoupling, gives a multiplet (Figure 1B) of which nine lines are clearly visible. If the zirconium were coupled equivalently to all 16 protons, one would anticipate a 17-line spectrum with relative intensities 1:16:120:560:1820:4368:8008:11440:12870:11440:8008:4368:1820:560:120:16:1. This intensity ratio range of $>10^4$ precludes observation of the weak outer lines, but the relative peak intensities are entirely consistent (see Figure 2A) with a 17-line spectrum with $J_{\mathrm{obsd}} = 28$ Hz. The appropriate satellite lines are also visible in the $^{1}$H spectrum, verifying the observed coupling constant.

The $^{11}$B spectrum of $Zr(BH_4)_4$ is a quintet ($J_{^{11}\mathrm{B}-\mathrm{H}} = 90$ Hz) centered at −8.0 ppm with respect to $Et_2O{\cdot}BF_3$. The proton-decoupled spectrum clearly shows the outer four of the six satellite lines due to coupling ($J_{^{91}\mathrm{Zr}-^{11}\mathrm{B}} = 18$ Hz) to the central nucleus which has a spin of $^5/_2$. One would thus anticipate for the $\{^1H\}^{91}$Zr spectrum a 13-line pattern with intensities 1:4:10:20:31:40:44:40:31:20:10:4:1 appropriate for coupling to four $^{11}$B nuclei. The situation is complicated by the superposition of a 70-line spectrum arising from the 40.3% of molecules in which the $^{91}$Zr is coupled to three $^{11}$B nuclei and one $^{10}$B nucleus ($I = 3$). Now, with use of the value of 18 Hz for $J_{^{91}\mathrm{Zr}-^{11}\mathrm{B}}$ obtained from the $\{^1H\}^{11}$B spectrum and a consequent $J_{^{91}\mathrm{Zr}-^{10}\mathrm{B}}$ value of ~6 Hz, the calculated and experimental $\{^{11}B\}^{91}$Zr spectra are compared in Figure 2B.

When both $^{1}$H and $^{11}$B are decoupled, the $^{91}$Zr spectrum is now reduced to a singlet (Figure 1D) positioned on a broad hump (Half-width ~40 Hz) attributable to a septet ($J_{^{91}\mathrm{Zr}-^{10}\mathrm{B}} = 6$ Hz; the singlet, which shows a very small isotope shift to low frequency, is the narrowest line (half-width 5 Hz) yet obtained in $^{91}$Zr NMR spectroscopy.

The observation of Zr–H spin–spin coupling is consonant either with the absence of exchange between bridging and terminal hydrogens or with a very rapid *intramolecular* exchange process. To be consistent with the experimental results, the former explanation also requires that the chemical shift difference between the bridging and terminal hydrogens be very small and that these protons couple equivalently to the boron. Arguments against such an eventuality have been marshalled by Marks[5] who has also obtained evidence for two exchange processes in the solid state.[6]

Rotation of the borohydride group must be accompanied by breaking of Zr–H bonds. Nevertheless, coupling between Zr and H will be retained providing that the spin state of the $H_4$ group is maintained during a rotation. Thus considering only a single borohydride moiety, the rate process will average the lines in the $^{91}$Zr spectrum associated with the $\alpha\alpha\alpha\beta$, $\alpha\alpha\beta\alpha$, $\alpha\beta\alpha\alpha$, and $\beta\alpha\alpha\alpha$ hydrogen spin states but will not average these lines with other lines arising from $H_4$ spin states with different numbers of $\alpha$ and $\beta$ spins, e.g., $\alpha\alpha\beta\beta$. It can be easily shown that this averaging will lead to a 17-line $^{91}$Zr spectrum with a $(3J_{\mathrm{bridging}} + J_{\mathrm{terminal}})/4$ splitting and a six-line $^{1}$H satellite spectrum with the same splitting. Now, if one assumes that $^{3}J_{\mathrm{Zr-H}}$ is very small, then it follows that $^{1}J_{\mathrm{Zr-H}} \approx 37$ Hz.

There are precedents in the literature for the retention of coupling constants during intramolecular bond-breaking processes. We note in this context the ESR results of DeBoer and Mackor[7] on ion pairing between $K^+$ and the pyracene radical anion and also the NMR data of MacLean and Mackor[8] on the protonated hexamethylbenzene cation, in anhydrous HF, which exhibits a 19-line multiplet, indicating coupling to 18 equivalent hydrogens. It seems reasonable that the spin orientation of the mobile group will be retained if the electron pairing is not disrupted in the bond-breaking process; this situation will thus be in accord with the Wigner spin conservation rule.[9]

## Experimental Section

Following the procedure of James and Smith,[10] $Zr(BH_4)_4$ was prepared from $ZrCl_4$ and $LiBH_4$ in an ether slurry. The product was purified by repeated trap-to-trap distillations and dissolved in toluene-$d_8$ freshly distilled from sodium.

The $^{91}$Zr spectra of an approximately 2 M solution of $Zr(BH_4)_4$ in toluene-$d_8$ were obtained at 8.37 MHz on a Bruker WH90 spectrometer operating at 25 °C. Typically, spectral widths of 3000 Hz in 4K of real data memory (0.73 Hz per point) and 90° (35 μs) pulses were used throughout. Up to 40 000 scans were required to provide adequate signal to noise. $Zr(BH_4)_4$ resonates at 40.7 ppm to high frequency of $(C_5H_5)_2ZrBr_2$. The $^{11}$B spectrum was obtained on the same instrument at 28.875 MHz. With proton decoupling, 16 scans (0.73 Hz per point) were required to observe $^{11}$B–$^{91}$Zr coupling. The proton spectrum was obtained on a Bruker WP80 spectrometer operating under standard conditions; 200 scans were required to observe $^{91}$Zr–H coupling.

The principles of tuning and matching of the decoupling coil are well-known.[11] The method adopted here was to remove all tuning elements from inside the probe and mount new single tuned and double tuned networks inside small brass containers which could then be

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attached separately via two BNC connectors to the base of the probe. A General Radio 1164-A frequency synthesizer, locked to a 5-MHz source from the spectrometer, and an RF Communications Inc. Type 805 amplifier were used to decouple $^{11}B$. Facility for proton decoupling was already available with the instrument.

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**Registry No.** $Zr(BH_4)_4$, 12370-59-1.

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# Base Hydrolysis of Resolved Halogeno- and Azido[2,6-bis(aminomethyl)pyridine](1,3-diamino-2-propanol-*N*,*N'*)cobalt(III) Ions. The Question of $\pi$ Stabilization in the $S_N1cB$ Mechanism

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*Received August 25, 1980*

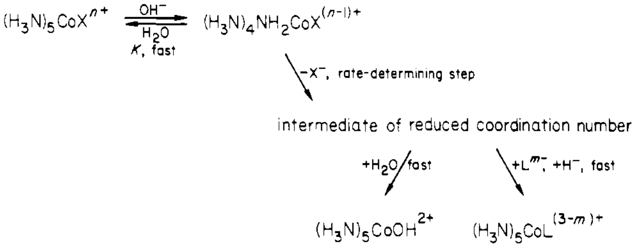
Some new optically active Co(III) pentaamine complexes have been synthesized that are specifically designed to test whether in the base hydrolysis reaction a trigonal bipyramid or a square pyramid is the preferred intermediate state following loss of the leaving group. In these species, a prochiral bidentate ligand is used to see whether its unique symmetry plane coincides with a plane of symmetry in the intermediate. Such coincidence is anticipated if the intermediate is a $\pi$-stabilized trigonal bipyramid. $[Co(bamp)(dapo)X]^{2+}$ ions (bamp = 2,6-bis(aminomethyl)pyridine, dapo = 1,3-diamino-2-propanol, X = $Cl^-$, $Br^-$, $N_3^-$) were resolved with use of dibenzoyltartaric acid. Their optical purity (≥97%) was established by interrelating independently resolved species by known stereoretentive reactions. Base hydrolysis (X = $Cl^-$, $k_{OH} = 2.9 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$; X = $Br^-$, $k_{OH} = 1.6 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$; 25 °C, $\mu = 1.0$) occurs with full retention of configuration at Co(III). In $N_3^-$ solution (1 mol dm$^{-3}$), the base hydrolysis reaction produces ~4% azido complex from the chloro and bromo complexes. $[2p(N) \rightarrow 3d_{x^2-y^2}(Co)]$ $\pi$ stabilization is not considered significant in the intermediate state after loss of the leaving group; certainly its lifetime is not appreciably lengthened by such bonding. This result is attributed to the inability of pyridine $\pi$ orbitals to give significant bonding. The possibility of $[3d_{xy}(Co) \rightarrow \pi^*(\text{pyridine})]$ back-bonding in stabilizing a square-pyramidal intermediate state is discussed.

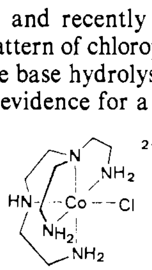
## Introduction

The base hydrolysis of Co(III) amine complexes is the object of extensive study,[2-4] and Scheme I shows a currently widely accepted mechanism. The proposal of a short-lived intermediate of reduced coordination number is based on stereochemical criteria,[5] on the results of competition experiments,[5,6] and on the observation of steric acceleration by increasingly bulky alkylamine ligands.[7] More recently, however, similar stereochemical[8,9] and competition studies,[8-10] carried out over an extended range of pentaamine structures and differently charged leaving groups, revealed some leaving-group dependence of the substitution process, which was rationalized in terms of an $I_d$ mechanism.

A classical hypothesis interprets the accelerated loss of the leaving group from the deprotonated reactant as the consequence of $\pi$-orbital overlap of the type $[2p(\text{deprotonated nitrogen}) \rightarrow 3d_{x^2-y^2}(Co(III))]$.[11] This model predicts that stabilization from this source will develop as the leaving group is being removed and it will reach its maximum in the five-coordinate intermediate if its configuration is trigonal bipyramidal and if the deprotonated nitrogen adopts a planar configuration with the nodal plane of its 2p orbital acting as a symmetry plane of the molecule. This proposal has been used to interpret the stereochemical course of various base hydrolysis reactions[12] and recently to rationalize the base hydrolysis reactivity pattern of chloropentaamine complexes.[13] On the other hand, the base hydrolysis reaction of $[Co(\textit{sym}\text{-trenen})Cl]^{2+}$ gave no evidence for a planar configuration of the secondary amine nitrogen, which is considered to be deprotonated in the reactive conjugate base.[14] While this ex-

Scheme I. The Proposed $S_N1cB$ Mechanism for Co(III) Pentaamine Base Hydrolysis[4-6]





$[Co(\textit{sym}\text{-trenen})Cl]^{2+}$

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