ondary importance, since the donor π orbital of the substituent is too far removed in energy from ψ_{-s} for efficient interaction and its π^* orbital is primarily localized on the phosphorus or arsenic rather than the nitrogen attached to the ring. The transition $\psi_a \rightarrow \psi_{-s}$, polarized perpendicular to the substituent–ring bond, should thus occur roughly at the same energy as in $S_3N_3^-$ itself.

Inspection of Figure 1 suggests that ψ_s' is indeed destabilized considerably relative to ψ_a and that the 20 500 cm^{-1} transition corresponds to the $\psi_s' \rightarrow \psi_{-s}'$ transition, in agreement with our tentative assignment of its polarization direction from the stretched-sheet measurement. The second transition (30 000 cm^{-1}), which occurs at almost the same energy as in $S_3N_3^-$ itself, is then assigned to the $\psi_a \rightarrow \psi_{-s}'$ excitation.

The signs of the observed *B* terms agree with the assignment of the two transitions in question to the two perimeter MO excitations ($\psi_a \rightarrow \psi_{-s}'$ and $\psi_s' \rightarrow \psi_{-s}'$). The *B* term of the first transition is given approximately[2] by

$$B_1/D_1 = -[\mu^-(2N + 2, N)](W_2 - W_1)^{-1}$$

where the magnetic moment $\mu^-(2N + 2, N)$ is characteristic of the $S_3N_3^-$ ring and $W_2 - W_1$ is the energy difference of the two transition energies. Using the experimental values of B_1, D_1, and $W_2 - W_1$, we find $\mu^- \simeq 0.8\ \mu_B$. In $S_3N_3^-$ we found[1a] $\mu^- = 0.98\ \mu_B$. To the extent that the excited state is represented by the pure $\psi_a \rightarrow \psi_{-s}$, $\psi_s \rightarrow \psi_{-s}$ pair of configurations, this is equal to the magnetic moment of an electron in the complex HOMO of $S_3N_3^-$. Alternatively, it can be viewed as the magnetic dipole transition moment between ψ_a and ψ_s. In **1** and **2**, the physical significance of μ^- is magnetic transition dipole moment between the first and second excited states. As long as these are each reasonably represented by a single configuration, this is equal to the magnetic dipole transition moment between orbitals ψ_a and ψ_s'. Since ψ_s' is somewhat delocalized onto the substituent and since only that part of it that lies on the ring contributes significantly to magnetic moments, it is quite reasonable that μ^- should be a little smaller in **1** and **2** than in $S_3N_3^-$ itself, as is found.[9]

In conclusion, we believe to have identified the lowest two perimeter states[2,10] in **1** and **2**, B_1 and B_2, and we find that the signs and magnitudes of their *B* terms agree with expectations based on the perimeter model.

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Registry No. **1**, 33082-06-3; **2**, 63212-45-3.

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Linkage Isomers of 5-Methyl- and 5-Phenyltetrazolato(1−) Complexes of Pentaamminecobalt(III) and Their Isomerization Reactions

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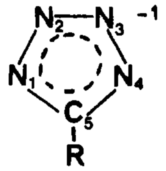
Tetrazoles and substituted tetrazoles have been investigated as the ligands of transition-metal complexes for several years. The cyclic tetrazolato(1−) anion, HCN_4^-, is isoelectronic with the cyclopentadienyl anion and the imidazolato anion. Thus, several potential bonding modes exist for the ligand in coordination compounds. First, the anion could function as an η^5 π-bonding ligand. However, despite early realization of this possibility[1] no evidence for such a bonding mode exists for complexes prepared to date. Numerous σ-bonding possibilities exist for the ligand as well. The carbon atom of the ring, ring position 5, has been shown to function as the σ donor with Au(III).[2] However, with 5-substituted tetrazoles, which are the topic of this study, this potential binding site is eliminated. Finally, the nonequivalent ring nitrogens may serve as the donor atom. For 5-substituted tetrazolato complexes, both N_1-[3] and N_2-bonded[4] complexes have been verified for complexes of coordination number 4 or less. Nevertheless, linkage isomers of a particular complex have never been isolated although equilibrium mixtures of the N_1- and N_2-bonded forms have been detected in solution for several Pt(II) and Pd(II) complexes.[5] Six-coordinate Co(III) complexes of 5-substituted tetrazoles have been recently reported[6] with bonding occurring exclusively via the N_2 donor. Although the N_1 nitrogens of 5-substituted tetrazolato anions are more nucleophilic than the N_2 nitrogens,[6a] it has been suggested that steric crowding of the substitutent at ring position 5 with the four groups cis to the tetrazole ligand, especially if the cis groups are sterically demanding, obviates N_1 coordination in octahedral complexes.[6a]



tetrazolato ring and numbering scheme

Tetrazoles with substituents at ring position 5 are conveniently prepared from organonitriles via nucleophilic attack of azide ion by a 1,3-dipolar cycloaddition reaction.[7] Coordination of organonitriles to the pentaamminecobalt(III) moiety is known to enhance the susceptibility of the nitrile carbon to nucleophilic attack by hydroxide ion[8] and cyanide ion.[9] Therefore, we have explored the possible reactions of organonitriles coordinated to cobalt(III) with azide ion in aqueous solution. Given the well-known substitution inertness of low-spin cobalt(III), an N_1-bonded tetrazolato complex would be expected if such attack were to occur. Direct substitution of 5-substituted tetrazoles for water in the aquopentaamminecobalt(III) complex has been shown by Lieberman et al.[6b] to yield N_2-substituted tetrazoles exclusively. Therefore, the synthetic approach employing formation of the 5-substituted

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tetrazolato ligand on the cobalt(III) center would yield the linkage isomers of Lieberman's complexes. We report here the unambiguous synthesis of 5-substituted (tetrazolato)pentaamminecobalt(III) complexes bonded at the N_1 nitrogen by the facile attack of azide ion on coordinated nitriles and the slow isomerization of the N_1 complexes to their N_2 linkage isomers.

Results and Discussion

When aqueous solutions of the pentaamminecobalt(III) complexes of acetonitrile or benzonitrile are treated with an excess of sodium azide at pH 5–6 (to prevent base hydrolysis to the amido complex[8]), significant spectral changes occur over the next few hours in the visible–near-ultraviolet region. However, isosbestic behavior is not observed, and if the reaction progress is monitored at a single wavelength in the near-ultraviolet region, clear indications of a two-step reaction are obtained.

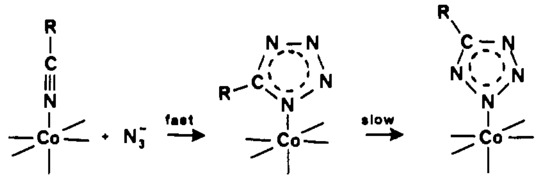
Cation-exchange chromatography of reaction mixtures on SP-Sephadex (a strong acid cation-exchange resin) indicates only one cobalt(III) species is present after overnight reaction of the nitrile complex with azide. The complex obtained has elution properties characteristic of a species with a charge of 2+. Precipitation of the product eluted from the ion-exchange column with sodium iodide yields a microcrystalline yellow-orange salt indicative of a nitrogen-bonded complex. Infrared vibrations in the 900–1100-cm^{-1} region typical of the tetrazole ring[10] are clearly present, and elemental analyses of the solids are consistent with the formulation of the products as (5-methyltetrazolato)- and (5-phenyltetrazolato)pentaamminecobalt(III) iodides (see Experimental Section). Infrared peaks due to either nitrile stretches or azide stretches are totally absent in the spectra.

In the case of the product obtained from the acetonitrile complex, assignment of an N_2 bonding mode has been possible since infrared, ultraviolet–visible and ^1H NMR spectral properties were identical with those reported by Lieberman et al.[6b] for their N_2-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex (see Experimental Section). Since the Sandia National Laboratories group did not synthesize a (5-phenyltetrazolato)pentaamminecobalt(III) complex, direct spectral comparison of this product to a known compound has not been possible. This product, however, has also been assigned an N_2 bonding mode for reasons discussed below.

Given the unexpected isolation of an N_2-bonded 5-methyltetrazolato complex, we then attempted to isolate the products from the first step of the two-step azide attack reaction, products that will hereafter be referred to as the initial products. In the case of the acetonitrile complex/azide ion reaction mixture, rapid precipitation of cobalt(III) complex after 2 h with sodium iodide yielded an initial product, while the benzonitrile reaction mixture was rapidly treated with sodium iodide after 15 min to yield an initial product. The products so obtained again showed infrared peaks in the tetrazole ring region, but the vibrations clearly differed in number, position, and intensity from those of the N_2-bonded final products. Here too, nitrile and azide group stretches were absent in the infrared. Elemental analyses of these initial products were again consistent with their formulation as (5-methyltetrazolato)- and (5-phenyltetrazolato)pentaamminecobalt(III) iodides (see Experimental Section).

Spectral comparisons in the infrared of the initial and final products of azide attack on coordinated acetonitrile and benzonitrile do show one consistent feature that bears upon their assigned bonding modes. The initial products exhibit sharp, medium to strong intensity absorptions at 1250 cm^{-1}, which are totally absent in the spectra of the final products. Lieber et al.[10] assign the peaks in this region to the cyclic unsubstituted –N—N=N configuration, a configuration that would be preserved in an N_1-bonded tetrazole complex but does not exist unsubstituted in an N_2-bonded complex due to the presence of the pentaamminecobalt(III) moiety.

Scheme I



The initial products are quite stable in the solid state but in aqueous solution are observed to undergo a reaction that after several hours results in complete conversion to the final product. Visible–near-ultraviolet spectral scans obtained during this time frame show isosbestic behavior, with isosbestic points occurring at 469, 382, and 342 nm for the acetonitrile complex/azide initial product reaction and at 479 nm for the benzonitrile complex/azide initial product reaction.

When they are taken together, these observations point to an initial formation of an N_1-bonded tetrazolato complex via azide attack on the coordinated nitrile carbon of a pentaamminecobalt(III) complex followed by or in concert with rapid ring closure to give the tetrazole ring as shown in step 1 of Scheme I. The observation that azide attack on coordinated benzonitrile occurs more rapidly than attack on coordinated acetonitrile parallels the results of base hydrolysis kinetic studies for coordinated nitriles, which show a rate constant for hydroxide attack at the nitrile carbon some 6 times faster in the case of benzonitrile[8a] vs. acetonitrile.[8b] Also, as with nucleophilic attack by hydroxide ion[8] and cyanide ion,[9] there is a considerable rate enhancement for azide attack on a coordinated vs. an uncoordinated nitrile. The formation of 5-methyltetrazole from sodium azide and acetonitrile requires a reaction time of 25 h at 150 °C[11] compared to only 2 h at ambient temperature for coordinated acetonitrile. Similarly, for benzonitrile the conditions are 3 h reaction time at 100 °C in dimethylformamide[7] vs. 15 min at ambient temperature for free and coordinated ligand, respectively.

The subsequent conversion of the N_1-bonded complex to an N_2-bonded complex, step 2 in Scheme I, in aqueous solution is directly verifiable in the case of the 5-methyltetrazolato complex since the N_2-bonded complex, the product of isomerization, has previously been synthesized by an independent route and characterized by Lieberman et al.,[6b] who verified the N_2 bonding mode of their pentaamminecobalt(III) compound via a single-crystal X-ray structure determination. The occurrence of similar visible spectral changes, similar infrared peak modifications, and similar reaction rates for the initial to final product conversions of the 5-phenyltetrazolato complex strongly indicates a similar interpretation, i.e., N_1 to N_2 isomerization, for the aqueous solution process observed. Additionally, a bathochromic shift in the ultraviolet region of the phenyl complex peak from 224 to 228 nm during the initial to final complex conversion and a concomitant intensity increase are observed. Such spectral modifications for aryltetrazoles have been interpreted as an indicator of increased conjugation between aromatic and tetrazolato ring systems as coplanarity is achieved.[12] An examination of molecular models indicates that coplanarity is attainable only for the N_2-bonded form of (5-phenyltetrazolato)pentaamminecobalt(III).

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The N_1 to N_2 linkage isomerization reaction appears to be driven by the steric congestion between the tetrazole ring substituent in the 5-position and the four cis ammines of the pentaamminecobalt(III) unit. An inspection of molecular models of the linkage isomers indicates that this congestion would be totally relieved in the N_2 bonding mode. Also consistent with the operation of a steric driving force is the observation that the N_1-bonded 5-phenyltetrazolato complex isomerizes some 6 times faster than the N_1-bonded 5-methyltetrazolato complex at 25 °C in 0.01 M perchloric acid with rate constants of 1.7×10^{-4} and 2.8×10^{-5} s^{-1}, respectively.[13]

Linkage isomerization reactions of cobalt(III) complex with ambidentate ligands are, of course, not unknown. There are, for example, the familiar nitrito to nitro conversion,[14] the S- to N-bonded thiocyanato isomerization,[15] and the N- to O-bonded formamido isomerization.[16] However, each of these linkage isomerizations involves a change in identity of the donor atom with electronic as well as steric forces contributing to the isomerization process.[17] Examples of linkage isomerizations involving like donor atoms are few. There is the amido nitrogen to nitrile nitrogen isomerization of coordinated *o*-cyanobenzamide,[18] but this facile reaction is thought to involve amido oxygen transfer and subsequent group rearrangement via a cyclic intermediate rather than a migration of the metal center.[19] Apparently the only similar linkage isomerization reported to date in the literature is the N_3 to N_9 isomerization of a pentaammineruthenium(III) hypoxanthine complex,[20] although electronic effects are thought to play a significant role in this isomerization reaction. As mentioned previously, a consideration of ring nitrogen nucleophilicity favors N_1 coordination for 5-substituted tetrazolato complexes,[6a] and hence, electronic considerations alone would predict no isomerization of the N_1-bonded tetrazolato complexes.

Experimental Section

Materials. All chemicals utilized in this study were reagent grade. Acetonitrile and benzonitrile were dried over 4-Å molecular sieves before use. Nitrile complexes of pentaamminecobalt(III) were prepared by a published procedure[21] involving the removal of the azide group of azidopentaamminecobalt(III) perchlorate[22] with $NOBF_4$ in triethyl phosphate followed by heating with the appropriate nitrile. Spectral properties of the acetonitrile[8b] and benzonitrile[8a] complexes agreed with literature values.

Physical Measurements. Spectroscopic data were obtained on the following instruments: infrared (KI pellets, 4000–200 cm^{-1}), Perkin-Elmer Model 599 spectrophotometer; ^1H NMR (in Me_2SO-d_6 vs. internal Me_4Si), Hitachi Perkin-Elmer Model R-600 60-MHz FT NMR; ultraviolet–visible, Cary 17 spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

Preparation of Complexes. (5-Methyltetrazolato)pentaamminecobalt(III) Iodide, N_1-Bonded Isomer, $[(NH_3)_5CoN_4C{-}CH_3]I_2{\cdot}1.5H_2O$. A 1-g quantity of $[(NH_3)_5CoNC{-}CH_3](ClO_4)_3$ was dissolved in a minimum volume of 1 M pH 5 acetate buffer (ca. 40 mL), and 5 g of sodium azide was added with stirring. *Caution*: operation near or below the pK_a of hydrazoic acid should be avoided due to the formation of toxic NH_3, i.e., pH 4.7. Stirring was continued for 2 h at room temperature at which time the solution was cooled in an ice bath and solid sodium iodide was added to induce rapid precipitation of the complex. The precipitated 5-methyltetrazolato complex obtained by filtration at this point invariably will contain some sodium azide impurity. Thus, the precipitate is redissolved in a minimum of water, chilled in an ice bath, and reprecipitated with sodium iodide. The precipitate was filtered, washed with ethanol and then ether, and dried in vacuo. As with all iodide salts prepared here, the complex must be protected from light in either an amber bottle or a vial wrapped with foil. Anal. Calcd for $CoC_2H_{18}N_9I_2{\cdot}1.5H_2O$: C, 4.73; H, 4.17; N, 24.82. Found: C. 4.71; H, 4.21; N, 24.81. UV-visible λ_{max}: 473 (ϵ 62 M^{-1} cm^{-1}); 335 nm (ϵ 77 M^{-1} cm^{-1}). ^1H NMR: δ 3.81 (cis NH_3's); 3.60 (trans NH_3); 2.58 ($-CH_3$).

(5-Phenyltetrazolato)pentaamminecobalt(III) Iodide, N_1-Bonded Isomer, $[(NH_3)_5CoN_4C{-}C_6H_5]I_2{\cdot}H_2O$. The preparation of the complex is achieved in a manner similar to the procedure above with 1 g of $[(NH_3)_5CoNC{-}C_6H_5](ClO_4)_3$ and 5 g of sodium azide dissolved in the pH 5 buffer. Due to the reduced solubility of this nitrile complex (vs. the acetonitrile complex), larger volumes of the buffer, ca. 125 mL, are required. Precipitation of the product with sodium iodide is initiated after only 15 min of stirring. Note: this tetrazolato complex isomerizes to the N_2 form more rapidly than the 5-methyl complex above, and hence, rapid precipitation and recrystallization are required. Anal. Calcd for $CoC_7H_{20}N_9I_2{\cdot}H_2O$: C, 14.98; H, 3.95; N, 22.47. Found: C, 14.91; H, 3.97; N, 22.41. UV-visible λ_{max} (H_2O): 472 (ϵ 69 M^{-1} cm^{-1}); 339 nm (ϵ 154 M^{-1} cm^{-1}). This complex isomerizes to the N_2-bonded linkage isomer very rapidly in Me_2SO-d_6 which precludes the acquisition of ^1H NMR data.

(5-Methyltetrazolato)pentaamminecobalt(III) Iodide, N_2-Bonded Isomer, $[(NH_3)_5CoN_4C{-}CH_3]I_2$. The N_2-bonded form of this complex is obtained in pure form if the procedure for the N_1 form is followed with stirring continued in excess of 30 h. More conveniently, heating of the reaction mixture on a steam bath for 2 h results in total conversion to the N_2-bonded isomer. Precipitation and recrystallization are carried out as described above for N_1 isomers although rapid precipitation is not of critical importance since the N_2-bonded linkage isomers do not isomerize. Anal. Calcd for $CoC_2H_{18}N_9I_2$: C, 4.99; H, 3.77; N, 26.21. Found: C, 5.11; H, 3.81; N, 26.09. UV–visible λ_{max} (H_2O): 465 (ϵ 64 M^{-1} cm^{-1}); 332 nm (ϵ 86 M^{-1} cm^{-1}) [lit.[6b] for the tetrafluoroborate salt: 464 (ϵ 64.8 M^{-1} cm^{-1}); 334 nm (ϵ 65.5 M^{-1} cm^{-1})]. ^1H NMR: δ 3.58 (cis and trans NH_3's); 2.52 ($-CH_3$) [lit.[6b]: δ 3.55; 2.45 (solvent unknown)].

(5-Phenyltetrazolato)pentaamminecobalt(III) Iodide, N_2-Bonded Isomer, $[(NH_3)_5CoN_4C{-}C_6H_5]I_2$. Complete conversion of the initially formed N_1-bonded complex to the N_2-bonded form will occur if the benzonitrile complex/sodium azide reaction mixture is stirred for 5 h or more at room temperature. Precipitation and recrystallization is performed as described above for N_1 isomers. Anal. Calcd for $CoC_7H_{20}N_9I_2$: C, 15.48; H, 3.71; N, 23.21. Found: C, 15.51; H, 3.71; N, 23.17. UV-visible λ_{max} (H_2O): 463 nm (ϵ 71 M^{-1} cm^{-1}). ^1H NMR: δ 7.77 (aromatic, center of multiplet); 3.64 (cis and trans NH_3's).

Perchlorate Salts. Attempts to obtain these complexes as perchlorate salts by precipitation with sodium perchlorate rather than sodium iodide invariably yielded complexes that analyzed as mixtures of protonated and deprotonated (3+ and 2+) complexes. Good elemental analyses for pure 2+ complexes could only be obtained if recrystallization was performed slowly and repeatedly. This procedure was, thus, impractical for the N_1-bonded forms of the complexes due to the linkage isomerization reaction. Nevertheless, a good analysis for the N_2-bonded form of the (5-phenyltetrazolato)pentaamminecobalt(III) complex, $[(NH_3)_5CoN_4C{-}C_6H_5](ClO_4)_2$, was obtained by this procedure following three recrystallizations. Anal. Calcd for $CoC_7H_{20}N_9Cl_2O_8$: C, 17.22; H, 4.10; N, 25.83. Found: C, 17.17; H, 4.10; N, 25.71.

Yields. Ion exchange of reaction mixtures on SP-Sephadex SP-C25-120 strong acid cation-exchange resin (Pharmacia Fine Chemicals, Inc.) after the reaction times specified above indicated that conversion of the nitrile complexes to their corresponding tetrazolato complex products was quantitative. Nevertheless, due to the greater solubility of the tetrazole products in aqueous solution (vs. their nitrile complex precursors), actual yields of isolated solid products invariably fell in the 35–55% of theoretical range.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical

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Society, for support of this research. W.R.E. acknowledges the receipt of a Robert E. Maytag fellowship administered by the University of Miami.

Registry No. $[(NH_3)_5CoN_4C{-}CH_3]I_2$, N_1-bonded isomer, 79899-66-4; $[(NH_3)_5CoN_4C{-}C_6H_5]I_2$, N_1-bonded isomer, 79899-67-5; $[(NH_3)_5CoN_4C{-}CH_3]I_2$, N_2-bonded isomer, 79899-68-6; $[(NH_3)_5CoN_4C{-}C_6H_5]I_2$, N_2-bonded isomer, 79899-69-7; $[(NH_3)_5CoN_4C{-}C_6H_5](ClO_4)_2$, N_2-bonded isomer, 79899-71-1; $[(NH_3)_5CoNC{-}CH_3](ClO_4)_3$, 15663-50-0; $[(NH_3)_2CoNC{-}C_6H_5](ClO_4)_3$, 38363-82-5; sodium azide, 26628-22-8.

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Tetraamine Complexes of Chromium(III). 3. Activation Parameters of the Aquation of *cis*-Aquachloro- and *cis*-Aquabromobis(ethylenediamine)chromium(III) Cations

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Received June 15, 1981

Although the aquation reactions of *cis*-aquachloro- and *cis*-aquabromobis(ethylenediamine)chromium(III) cations have been studied many years ago,[1–5] the activation parameters of these reactions have not been reported. Only Bratushko and Nazarenko[3] gave an activation energy of 25.1 kcal mol^{-1} (105 kJ mol^{-1}) for the aquation of *cis*-aquachlorobis(ethylenediamine)chromium(III) cation, but they studied this reaction in water instead of in acidic solutions so their value might include activation energy of base hydrolysis. In this note the activation parameters of the aquation of *cis*-aquachloro- and *cis*-aquabromobis(ethylenediamine)chromium(III) cations in perchloric acid are reported.

Experimental Section

cis-Aquachlorobis(ethylenediamine)chromium(III) bromide hydrate and *cis*-aquabromobis(ethylenediamine)chromium(III) bromide hydrate were prepared and analyzed by methods previously reported.[6–8] All other chemicals used were reagent grade, and sodium perchlorate was prepared as previously reported.[9]

The rates of aquation were determined spectrophotometrically by following the decrease in the absorbance at 520 nm, with use of procedures previously reported.[8,10] The rate constants were evaluated from the initial slopes of plots of ln $(A_t - A_\infty)$ vs. time.

Results and Discussion

The pseudo-first-order rate constants for the aquation of *cis*-aquachloro- and *cis*-aquabromobis(ethylenediamine)chromium(III) cations are summarized in Table I. Each reaction was studied at three different temperatures in order to evaluate the activation parameters; and the reactions were also studied in two different acid concentrations, 0.10 and 1.0 M perchloric acid (μ = 1.0, $NaClO_4$), in order to observe any possible effect of changing acid concentration.

Table I. Pseudo-First-Order Rate Constants for the Aquation of the *cis*-$[CrCl(H_2O)(en)_2]^{2+}$ and *cis*-$[CrBr(H_2O)(en)_2]^{2+}$ Cations (μ = 1.0, $NaClO_4$)

T, °C	[H$^+$], M	10^5k_{Cl}, s^{-1}	10^4k_{Br}, s^{-1}
25	0.10		1.75
	1.0		1.60
30	0.10	3.90	2.90
	1.0	3.77	2.69
35	0.10	7.15	4.73
	1.0	7.21	4.43
40	0.10	12.5	
	1.0	12.6	

Table II. Activation Parameters for the Aquation of the *cis*-$[CrCl(H_2O)(en)_2]^{2+}$ and *cis*-$[CrBr(H_2O)(en)_2]^{2+}$ Cations (μ = 1.0, $NaClO_4$)

[H$^+$], M	$\Delta H_{Cl}^{\ddagger}$, kJ mol^{-1}	$\Delta S_{Cl}^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta H_{Br}^{\ddagger}$, kJ mol^{-1}	$\Delta S_{Br}^{\ddagger}$, J K^{-1} mol^{-1}
0.10	88.8 ± 0.7[a]	−36.5 ± 2.2[a]	73.3 ± 0.2[a]	−70.8 ± 0.6[a]
1.0	92.1 ± 1.8	−25.7 ± 0.6	75.2 ± 0.5	−65.5 ± 1.5

[a] The error is the standard deviation evaluated from the least-squares analysis.

For the aquation of the *cis*-$[CrCl(H_2O)(en)_2]^{2+}$ cation, there is no effect on changing acid concentration within experimental error. Comparison of rate constants with literature values cannot be successfully made since the reaction conditions were different. Selbin and Bailar[1] found a rate constant of 2.8 × 10^{-5} s^{-1} in 0.10 M $HClO_4$ at 25 °C, and the extrapolated value of this work at 25 °C is 2.41 × 10^{-5} s^{-1}. MacDonald and Garner[2] reported a rate constant of 9.23 × 10^{-5} s^{-1} in 0.10 M HNO_3 at 35 °C; however, the rate constant found in this work in 0.10 M $HClO_4$ (μ = 1.0) at 35 °C is 7.15 × 10^{-5} s^{-1}. The difference might be caused by the difference in the acid used since MacDonald and Garner[2] also found a rate constant in 1.3 M HNO_3 about 2.5 times that in 0.10 M HNO_3 while the rate constant in 1.0 M $HClO_4$, found in this work, is similar to that in 0.10 M $HClO_4$ (μ = 1.0). They attributed the high rate constant to ion-pair formation, but nitrate-catalyzed acceleration of the reaction rate is also possible.

For the aquation of the *cis*-$[CrBr(H_2O)(en)_2]^{2+}$ cation, there seems to be a slight effect of changing acid concentration on the rate; and there is a definite trend in the deviation, that is, toward smaller rate constant in higher acid concentration. This behavior is also observed in the aquation of the *cis*-aquabis(ethylenediamine)iodochromium(III) cation,[11] and the deviation of rate constant with changing acid concentration in this reaction is even larger than that in the aquation of the *cis*-aquabromo complex. Slight base hydrolysis in lower acid concentration is suspected, but any suggestion to explain this behavior cannot be made until the study of the aquation of the *cis*-$[CrI(H_2O)(en)_2]^{2+}$ cation is completed. The rate constant found for the aquation of the *cis*-$[CrBr(H_2O)(en)_2]^{2+}$ cation in this work, 1.75 × 10^{-4} s^{-1} in 0.10 M $HClO_4$ (μ = 1.0) at 25 °C, agrees well with those reported in the literature under similar conditions (1.70 × 10^{-4} s^{-1} in 0.4 M $HClO_4$ at 25 °C[5] and 2.0 × 10^{-4} s^{-1} in 0.0725 M $HClO_4$ at 24.8 °C[4]).

The activation parameters for the aquation of the *cis*-aquachloro- and *cis*-aquabromobis(ethylenediamine)chromium(III) cations are listed in Table II. The enthalpies of activation are similar in magnitude to many other aquation reactions of chloro- and bromobis(ethylenediamine) complexes of Cr(III).[5,10] The entropies of activation are negative for both reactions, also similar to those for the aquation of other chloro and bromo systems.[5,10] It is of interest to note that the ac-

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