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

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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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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 ($A_t - A_∞$) 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, NaClO₄), in order to observe any

Table I. Pseudo-First-Order Rate Constants for the Aquation of the *cis*-[CrCl(H₂O)(en)₂]²⁺ and *cis*-[CrBr(H₂O)(en)₂]²⁺ Cations (μ = 1.0, NaClO₄)

T, °C	[H⁺], M	$10^5 k_{Cl}$, s⁻¹	$10^4 k_{Br}$, 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(H₂O)(en)₂]²⁺ and *cis*-[CrBr(H₂O)(en)₂]²⁺ Cations (μ = 1.0, NaClO₄)

[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 ± 0.7ᵃ	−36.5 ± 2.2ᵃ	73.3 ± 0.2ᵃ	−70.8 ± 0.6ᵃ
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.

possible effect of changing acid concentration.

For the aquation of the *cis*-[CrCl(H₂O)(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 HClO₄ 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 HNO₃ at 35 °C; however, the rate constant found in this work in 0.10 M HClO₄ (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 HNO₃ about 2.5 times that in 0.10 M HNO₃ while the rate constant in 1.0 M HClO₄, found in this work, is similar to that in 0.10 M HClO₄ (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(H₂O)(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(H₂O)(en)₂]²⁺ cation is completed. The rate constant found for the aquation of the *cis*-[CrBr(H₂O)(en)₂]²⁺ cation in this work, 1.75 × 10⁻⁴ s⁻¹ in 0.10 M HClO₄ (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 HClO₄ at 25 °C[5] and 2.0 × 10⁻⁴ s⁻¹ in 0.0725 M HClO₄ 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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tivation parameters for the aquation of the *cis*-aquachlorobis(ethylenediamine)chromium(III) cation, calculated by using the literature values (2.8 × 10^{-5} s^{-1} in 0.1 M HClO$_4$ at 25 °C,[1] 5.0 × 10^{-5} s^{-1} in 0.055 M HClO$_4$ at 30 °C,[3] and 9.23 × 10^{-5} s^{-1} in 0.1 M HNO$_3$ at 35 °C[2]), namely, $\Delta H^* = 88.5 \pm 1.1$ kJ mol^{-1} and $\Delta S^* = -35.2 \pm 3.7$ J K^{-1} mol^{-1}, are similar to those found in this work.

Registry No. *cis*-[CrCl(H$_2$O)(en)$_2$]$^{2+}$, 14403-89-5; *cis*-[CrBr(H$_2$O)(en)$_2$]$^{2+}$, 60429-48-3.

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NMR Evidence for Thermodynamic Preference of Cis(N,olefin) over Trans(N,olefin) Isomers of Mixed Amino Acid–Olefin Complexes of Platinum(II)

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Though both trans(N,olefin) and cis(N,olefin) isomers of [Pt(amino acid)(olefin)Cl] have been reported, the relative stability of the isomers has not been previously determined. Synthetic routes have been used to obtain the separate isomers on the basis of relative trans effects of ethylene and Cl$^-$. Reactions of amino acid anions with Zeise's salt yield the trans(N,olefin) isomers exclusively,[1,2] while the cis isomers have been obtained by olefin displacement of chloride from [Pt(H-amino acid)Cl$_3^-$] in which the amino acid is N-coordinated and protonated.[3]
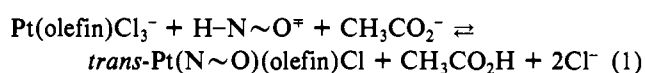
Our interest in the thermodynamic preference of these isomers originated in our earlier work on corresponding mixed amino acid–Me$_2$SO complexes, for which the cis(N,S) isomers are strongly preferred for simple amino acids like glycine, alanine, and α-aminoisobutyric acid (aba).[4,5] In view of the similar trans influence of Me$_2$SO and ethylene, it seemed likely that the cis isomer of the olefin complexes might also be preferred.[6,7]

After initial unsuccessful attempts to equilibrate trans isomers of ethylene complexes in H$_2$O and in some nonaqueous solvents, we turned our attention to the water-soluble olefins, allyl alcohol and allylsulfonate. Published equilibrium constants for the formation of Zeise's salt analogues of these ligands from PtCl$_4^{2-}$ ensure essentially complete conversion of PtCl$_4^{2-}$ to Pt(olefin)Cl$_3^-$ for the equimolar mixtures of olefin and PtCl$_4^{2-}$ in aqueous solution.[8] On addition of weak base
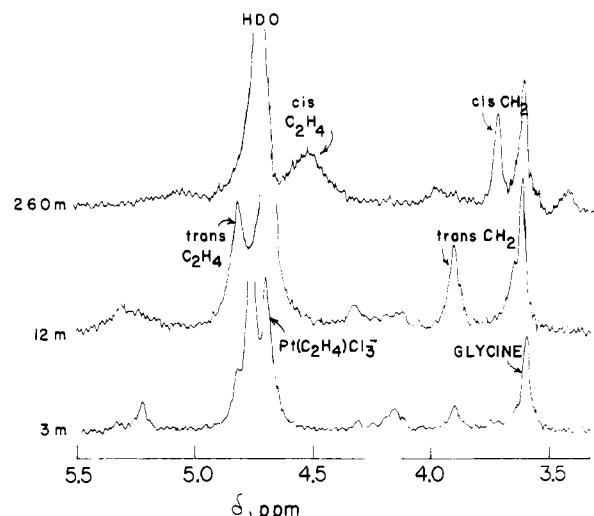
Figure 1. Proton NMR spectra as a function of time for 0.30 M KPt(C$_2$H$_4$)Cl$_3$, 0.30 M glycine, and 0.30 M sodium acetate showing rapid formation of *trans*(N,ethylene)-chloro(glycine)(ethylene)platinum and subsequent slow conversion to cis isomer.

(acetate) and the neutral zwitterionic amino acid to such solutions, the following equilibrium is rapidly established (where N~O denotes the amino acid anion):

$$\text{Pt(olefin)Cl}_3^- + \text{H-N}\sim\text{O}^\mp + \text{CH}_3\text{CO}_2^- \rightleftharpoons$$
$$\textit{trans-}\text{Pt(N}\sim\text{O)(olefin)Cl} + \text{CH}_3\text{CO}_2\text{H} + 2\text{Cl}^- \quad (1)$$

Equilibration to the cis isomer, reaction 2, can then occur either

$$\textit{trans-}\text{Pt(N}\sim\text{O)(olefin)Cl} \rightleftharpoons \textit{cis-}\text{Pt(N}\sim\text{O)(olefin)Cl} \quad (2)$$

via stepwise displacement and subsequent reverse addition of amino acid to Pt(olefin)Cl$_3^-$ or by other pathways involving Cl$^-$ displacement of olefin or Cl$^-$ catalysis. The presence of the acetate ion ensures that the aqueous solutions are buffered in the pH 4–5 region when equilibrium is established. Thus hydrolysis of Cl$^-$ or ring opening of the amino acid chelate by carboxyl protonation are not significant side reactions. Proton NMR spectroscopy has been used to follow the spectral changes associated with reactions 1 and 2. Though the technique was developed for the water-soluble olefins, equilibration of ethylene complexes was also successfully followed by the same approach.

Experimental Section

Reagents were all commercially available and were used without purification except for sodium allylsulfonate, which was synthesized by the reaction of sodium sulfite with allyl bromide.[9] Proton NMR spectra were recorded with a Perkin-Elmer R-12 NMR spectrometer.

Kinetic Runs. Stock solutions of Pt(olefin)Cl$_3^-$ were prepared by adding the olefin and K$_2$PtCl$_4$ in a 1:1 mole ratio to D$_2$O. The formation of the 1:1 complex was monitored by NMR spectral changes and by color changes (red to yellow). A similar solution containing a 1:1 ratio of amino acid and acetate was also prepared. However, in order to avoid excess dilution of final solutions, a stochiometric quantity of this amino acid–acetate solution was rotary evaporated to dryness and the Pt(olefin)Cl$_3^-$ solution was added to this dry solid to initiate reaction 1. For Pt(ethylene)Cl$_3^-$ reactions, 0.30 mmol of Zeise's salt was dissolved in 1 mL of D$_2$O containing 0.30 M amino acid and 0.30 M sodium acetate. Spectral changes associated with subsequent equilibration of trans and cis isomers were monitored until no further changes were observed.

Analyses. Most of the complexes were quite soluble in water and were not actually isolated. However, *cis*-Pt(aba)(allyl alcohol)Cl precipitated from the reaction mixtures. The isomer assignment was based on NMR data. Anal. Calcd for C$_7$H$_{14}$NO$_3$PtCl: C, 21.63; H, 3.11; N, 3.60. Found: C, 21.32; H, 3.59; N, 3.82.

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