they would be formed in either Me_2SO or $CHCl_3$.

The equilibrium constants for the formation of the pentacoordinate species are 0.83 for the chloride complex and 0.69 for the bromide complex. These values are lower than those found for the phenyldivinylphosphine[38] or 1-phenyl-3,4-dimethylphosphole complexes.[20] However, the values for the diphenyl(2-cyanoethyl)phosphine complexes are not particularly reliable since, due to their low solubility, precipitate was forming at low temperature during the NMR data acquisition.

There is a definite geometric aspect to ligand-exchange reactions of platinum phosphine complexes. For all the complexes studied herein, as well as other complexes previously studied,[20] if the trans isomer is thermodynamically more stable than the cis isomer, then the complex does not form pentacoordinate species with added ligand or isomerize to the cis isomer at elevated temperatures. If, as in the case of $(CEP)_2PtCl_2$, the cis isomer is only slightly thermodynamically more stable, then at higher temperatures the increase in entropy is sufficient to favor the trans isomer. However, if the trans isomer is slightly thermodynamically more stable than the cis isomer, then an increase in the entropy contribution to the free energy renders the isomerization to the cis isomer even less favorable.

The formation of pentacoordinate species also has a geometrical aspect. Both the dichlorotris(diphenyl(2-cyanoethyl)phosphine)platinum(II) and dibromotris(diphenyl(2-cyanoethyl)phosphine)platinum(II) complexes, herein shown to be pentacoordinate, when rewarmed to room temperature, re-form the respective cis isomer with no evidence of the trans isomer.

Thus, when the pentacoordinate species is sufficiently stable to be observed, only an equilibrium between *cis*-L_2PtX_2 and L_3PtX_2 is observed. In contrast, when *cis*- and *trans*-L_2PtX_2 have similar thermodynamic stabilities, cis–trans isomerization is observed and the pentacoordinate species become a transition state for the geometrical isomerization, and L_3PtX_2 is not spectroscopically observable. Combining the results of all the studies to date concerning L_3PtX_2 pentacoordinate platinum complexes suggests that ligand steric effects are dominant over electronic effects in stabilizing pentacoordinate complexes. Thus, when the neutral ligand L is sterically small, *cis*-L_2PtX_2 is uniformly thermodynamically more stable than the trans complexes. In this case, upon addition of excess L to a solution of *cis*-L_2PtX_2, the pentacoordinate L_3PtX_2 is detectable at low temperature. If the neutral ligand is slightly larger, then *cis*-L_2PtX_2 and *trans*-L_2PtX_2 have similar thermodynamic stabilities, and the reversible cis to trans geometrical isomerization is catalyzed by L, but no L_3PtX_2 pentacoordinate complexes may be spectroscopically observed. When L is still larger, the *trans*-L_2PtX_2 complexes increase in thermodynamic stability and the *cis*-L_2PtX_2 complex may be kinetically trapped by virtue of its synthesis. Then excess L catalyzes the unidirectional cis–trans isomerization, and again no pentacoordinate L_3PtX_2 complexes can be detected.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for partial financial support of this work.

Registry No. *cis*-$(CEP)_2PtCl_2$, 100838-88-8; *trans*-$(CEP)_2PtCl_2$, 20699-88-1; *trans*-$(CEP)_2PtBr_2$, 101166-31-8; *trans*-$(CEP)_2PtI_2$, 101166-32-9; *cis*-$(PhCEP)_2PtCl_2$, 101166-33-0; *cis*-$(PhCEP)_2PtBr_2$, 101166-34-1; *trans*-$(PhCEP)_2PtI_2$, 101166-35-2; *cis*-$(Ph_2CEP)_2PtCl_2$, 101166-36-3; *cis*-$(Ph_2CEP)_2PtBr$, 101166-37-4; *trans*-$(Ph_2CEP)_2PtI_2$, 101166-38-5; $[Ph_2CEP]_3PtCl_2$, 101166-39-6; $[Ph_2CEP]_3PtBr_2$, 101166-40-9; dichlorobis(benzonitrile)platinum(II), 14873-63-3.

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Kinetics of Aquation of Potentially Strained Chromium(III) Complexes Containing Tetradentate Macrocyclic Ligands

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The rate constants for the hydrolysis of *cis*- and *trans*-$[CrLCl_2]^+$ where L is cyclen (I) or isocyclam (III) have been determined in 0.1 M acid solution and have been compared with similar chromium(III) complexes containing other tetradentate ligands. The rate constants for the first aquation reaction have the following order (25 °C): *cis*-cyclen (7.6×10^{-2} s^{-1}) > *cis*-isocyclam (8.6×10^{-4} s^{-1}) > *cis*-cyclam (2.5×10^{-5} s^{-1})[4] and *trans*-isocyclam (5 s^{-1}) > *trans*-cyclam (2×10^{-8} s^{-1}).[4] The ratio of the rate constants for the aquation of *cis*-$[Cr(cyclen)Cl_2]Cl\cdot H_2O$ to *cis*-$[Cr(cyclam)Cl_2]Cl$ is 3040 to 1, while the ratio of rate constants for *cis*-$[Cr(isocyclam)Cl_2]Cl$ to *cis*-$[Cr(cyclam)Cl_2]Cl$ is 34.4 to 1. However, the ratio of rate constants for *trans*-$[Cr(isocyclam)Cl_2]Cl$ to *trans*-$[Cr(cyclam)Cl_2]Cl$ is approximately 4×10^7 to 1. The relative rates of reactions have been interpreted in terms of the bond strain imposed by the macrocycles and steric factors.

Introduction

Macrocyclic ligands bonded to first-row transition-metal ions are usually kinetically inert with respect to dissociation of the macrocyclic ligand from the metal ion.[1] As a result, six-coordinate chromium(III) and cobalt(III) complexes containing a tetradentate macrocyclic ligand will have only two sites that are susceptible to substitution by relatively weak nucleophiles such as water. The reactivity of these two sites is expected to be influenced by the nature of the macrocycle.

Busch and Hung[2] have shown that the rates of the first aquation of $[CoLCl_2]^+$ (L is a neutral tetraaza cyclic ligand) are parallel to the bond strain imposed by the macrocycle. Cobalt(III) complexes usually undergo substitution reactions by a D mechanism while chromium(III) complexes undergo substitution reactions by an A mechanism.[3] At present there have been no systematic studies comparing how various macrocyclic ligands can influence the rates of aquation of $[CrLCl_2]^+$.

Campi, Ferguson, and Tobe[4] have obtained kinetic data for the aquation of the *cis*- and *trans*-$[Cr(cyclam)Cl_2]^+$. We have prepared and characterized chromium(III) complexes containing a 12- and 15-membered saturated tetraaza cyclic ligands (I, II) and an unsymmetrical 14-membered saturated tetraaza cyclic ligand

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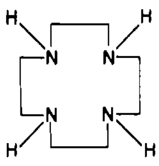
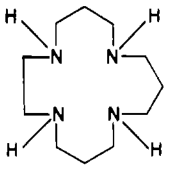
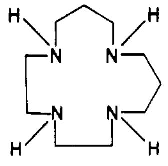
(III).[5] Strained metal-to-donor bonds are expected if the cavity in the macrocycle is either too small or too large for a given metal ion.[2,5-8] Also, unsymmetrical macrocycles bonded to a metal ion should result in strained ring conformations.[5,8] Therefore, metal ions containing relatively small (I), large (II), or unsymmetrical (III) tetradentate macrocycles are expected to be strained high potential energy complexes.


I (cyclen or [12]aneN$_4$)


II ([15]aneN$_4$)


III (isocyclam)

By comparing the rates of acid hydrolysis of the $[CrLCl_2]^+$ with those obtained by Campi, Ferguson, and Tobe,[4] we hope to be able to elucidate the factors influencing the rate of these reactions. All the chromium(III) complexes in which the rates of acid hydrolysis were measured have been previously prepared and characterized.[5]

Experimental Section

(A) Materials. Chromium(III) complexes were prepared according to literature procedures.[5]

(B) Kinetic Measurements. The kinetic measurements were followed spectrophotometrically with a Beckman Acta MIV spectrophotometer and a Gibson-Durrum stopped-flow spectrometer. The cell housing and solvent temperature was controlled with a HAAKE Model FX thermostat water bath. The reactions employing the Beckman Acta IV were followed in situ in a 1-cm cell. Three mL of 0.1 M HNO_3, previously brought to the reaction temperature, was added by syringe to a weighed amount of complex in the silica cell. This mixture was shaken and placed in the spectrophotometer. The wavelength range 700–350 nm was repeatedly scanned to obtain isosbestic points. Absorbance was recorded as a function of time at various temperatures to obtain the rate constant and activation parameters. Reactions were followed for 8–10 half-lives. The temperature was measured by inserting a thermometer into the cell at the end of the reaction.

Results

The visible spectrum of $[Cr(cyclen)Cl_2]Cl{\cdot}H_2O$ dissolved in 0.1 M HNO_3 changes with time. The isosbestic points at 425 and 540 nm indicate that either two metal-containing compounds are present (the starting material and product) or two products are formed in a constant ratio. The second possibility is unlikely. The visible spectrum of the product has absorbance maxima at 362 and 520 nm and is identical with the spectrum of $[Cr(cyclen)(H_2O)_2]^{3+}$ produced by the following method. A column of Amberlite IRC-50 cation-exchange resin was converted to the Na^+ form by passing aqueous 2 M $NaNO_3$ through the column until the effluent was no longer acidic to litmus paper. The column was then washed with 2 L of distilled water. Next a weighed amount of $[Cr(cyclen)Cl_2]Cl{\cdot}H_2O$ dissolved in water was adsorbed onto the column. After the complex had been adsorbed, it was eluted with distilled water. The effluent was titrated for chloride ions by the potentiometric method using standardized $AgNO_3$. The titration yielded 3.08 chlorides per molecule. This yield indicates that the species adsorbed on the column must be $[Cr(cyclen)(H_2O)_2]^{3+}$.[5] The $[Cr(cyclen)(H_2O)_2]^{3+}$ was then displaced from the column by passing 2 M $HClO_4$ through the column.[5]

The visible spectrum of the initial species formed in this aquation reaction has absorbance maxima at 382 and 547 nm. This species cannot be $[Cr(cyclen)Cl_2]^+$, which has absorbance maxima at 400 and 582 nm in methanol, nor can it be $[Cr(cyclen)(H_2O)_2]^{3+}$, which has bands at 362 and 520 nm. Therefore, we conclude that the initial complex is $[Cr(cyclen)Cl(H_2O)]^{2+}$. We also observed that the visible spectrum of an aqueous solution of $[Cr(cyclen)(H_2O)_2]^{3+}$ and 3 M sodium chloride has absorbance maxima at 385 and 550 nm. Therefore, the ion formed from the reaction of $[Cr(cyclen)(H_2O)_2]^{3+}$ and Cl^- is also $[Cr(cyclen)(H_2O)Cl]^{2+}$.

Table I. Rate Constants as a Function of Temperature for the Acid Hydrolysis of Chromium(III) Complexes[a]

T, K	k_{obsd}, s^{-1}	T, K	k_{obsd}, s^{-1}
First Aquation of *cis*-$[Cr(cyclen)Cl_2]Cl{\cdot}H_2O$			
280	2.2×10^{-2}	307	1.6×10^{-1}
292	4.6×10^{-2}	309	2.0×10^{-1}
298	6.2×10^{-2}	310	2.6×10^{-1}
Second Aquation of *cis*-$[Cr(cyclen)Cl_2]Cl{\cdot}H_2O$			
288	4.36×10^{-4}	318	4.69×10^{-3}
301	1.57×10^{-3}	333	1.44×10^{-2}
First Aquation of [*cis*-$Cr(isocyclam)Cl_2]Cl$			
301	1.12×10^{-3}	323	6.39×10^{-3}
313	3.36×10^{-3}	333	1.37×10^{-2}

[a] All complexes were dissolved in 0.1 M HNO_3.

Table II. First-Order Rate Constants and Activation Parameters for the Acid Hydrolysis of *cis*-$[Cr(N_4)Cl_2]^+$ and *trans*-$[Cr(N_4)Cl_2]^+$ Complexes at 25.0 °C

complex	k_H, s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	ref
cis-$[Cr(cyclen)Cl_2]^+$	7.6×10^{-2}	14.8	−14.1	*a*
cis-$[Cr(cyclam)Cl_2]^+$	2.5×10^{-5}	22.9	−5	*b*
cis-$[Cr(isocylam)Cl_2]^+$	8.6×10^{-4}	14.7	−23.2	*a*
cis-$[Cr(cyclen)(H_2O)Cl]^{2+}$	1.01×10^{-3}	14.2	−24.6	*a*
cis-α-$[Cr(2,2,2\text{-tet})Cl_2]^+$	1.9×10^{-4}	21	−6.6	*c*
cis-β-$[Cr(2,2,2\text{-tet})Cl_2]^+$	3.1×10^{-2} (0 °C)			*d*
cis-β-$[Cr(2,3,2\text{-tet})Cl_2]^+$	4.12×10^{-4}	17.7	−16.5	*e*
cis-β-$[Cr(3,2,3\text{-tet})Cl_2]^+$	1.02×10^{-4}	21.2	−7.6	*f*
trans-$[Cr(cyclam)Cl_2]^+$	2×10^{-8}	27	−1.9	*b*
trans-$[Cr(isocylam)Cl_2]^+$	5 (20 °C)			*a*

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It was possible to determine first-order rate constants for the second aquation reaction

$$cis\text{-}[Cr(cyclen)(H_2O)Cl]^{2+} \xrightarrow{k_2} cis\text{-}[Cr(cyclen)(H_2O)_2]^{3+}$$

from the slope of a plot of ln $(A_t - A)$ vs. time, where A = absorbance. The kinetics were measured at 580 nm because at this wavelength *cis*-$[Cr(cyclen)Cl(H_2O)]^{2+}$ and *cis*-$[Cr(cyclen)(H_2O)_2]^{3+}$ have the largest differences in exctinction coefficients. The rate constant (Table I) was determined at various temperatures. The plot of ln (k/T) vs. $1/T$ yielded an enthalpy of activation and the entropy of activation (Table II).

The first-order rate constant for the first aquation reaction

$$cis\text{-}[Cr(cyclen)Cl_2]^{+} \xrightarrow{k_1} cis\text{-}[Cr(cyclen)(H_2O)Cl]^{2+}$$

in 0.1 M HNO_3 was studied at 425 nm by measuring absorbance vs. time with the same techniques as above. The reason that we measured absorbance vs. time at 425 nm was because at this wavelength there exists an isosbestic point for the second aquation reaction. Therefore the second aquation reaction should not interfere with our determination of the rate constant for the first aquation reaction. The rate constants were determined for several temperatures (Table I), and a plot of ln (k/T) vs. $1/T$ yielded ΔH^* and ΔS^* values (Table II).

The visible spectrum of *cis*-$[Cr(isocyclam)Cl_2]Cl$ in 0.1 M HNO_3 was observed to change with time. The isosbestic points

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observed at 422, 477, and 542 nm suggest either that two metal-containing species are present (starting material and product) or that two products are formed in a constant ratio. The second possibility is unlikely. The first spectrum observed in solution had maximum absorbances at 432 and 545 nm. These maxima are similar to those of *cis*-$[Cr(isocyclam)Cl_2]Cl$ taken in the solid-state.[5] It was therefore concluded that the initial compound observed in the solution spectrum is *cis*-$[Cr(isocyclam)Cl_2]^+$. Conductivity data on an aqueous solution of *cis*-$[Cr(isocyclam)Cl_2]Cl$ approaches that of a 2:1 electrolyte within 1 h. Therefore, we conclude that the compound formed from *cis*-$[Cr(isocyclam)Cl_2]Cl$ is *cis*-$[Cr(isocyclam)(H_2O)Cl]Cl_2$. It is not likely that the reaction observed is a cis-to-trans isomerization since only two peaks in the visible spectrum were observed for the solution containing the product of the aquation reaction. The cis isomer is expected to have only two peaks in the visible spectrum.

First-order rate constants were obtained spectrophotometrically for the aquation reaction

$$cis\text{-}[Cr(isocyclam)Cl_2]^+ + H_2O \xrightarrow{k_1} cis\text{-}[Cr(isocyclam)(H_2O)Cl]^{2+} + Cl^-$$

Data were obtained by monitoring the absorbance at 450 nm as a function of time. A plot of ln $(A_t - A)$ vs. time was constructed at several temperatures to obtain first-order rate constants (Table I). ΔH^* and ΔS^* values (Table II) were obtained in the same manner as already discussed.

The conductivity data of *trans*-$[Cr(isocyclam)Cl_2]Cl$ in nitromethane are within the expected range for a 1:1 electrolyte. However, the conductivity of a freshly prepared sample of *trans*-$[Cr(isocyclam)Cl_2]Cl$ in water is in the range for a 2:1 electrolyte, indicating that the coordination sphere of the chromium contains the isocyclam, one chloride, and one water. In order to obtain the rate constant for the first aquation reaction for *trans*-$[Cr(isocyclam)Cl_2]Cl$, the stopped-flow method was employed. Two solutions were prepared—one solution was the complex dissolved in methanol and the other was an aqueous solution containing 0.2 M HNO_3. These solutions were mixed in the stopped-flow apparatus. The reaction was followed at 462 nm. A large error in rate constant was expected because of poor mixing of the two solvents in the stop-flow apparatus. The estimated rate constant at 20.0 °C is 5 s^{-1}.

The rate of aquation of *trans*-$[Cr([15]aneN_4)Cl_2]Cl\cdot 2H_2O$ is very slow. Conductivity data indicated that an aqueous solution of *trans*-$[Cr([15]aneN_4)Cl_2]Cl$ is initially a 1:1 electrolyte, thereby indicating that two chlorides are coordinated to chromium(III) in solution. After this solution was allowed to stand at room temperature for 3 days, its molar conductivity approached that of a 2:1 electrolyte. A 2:1 electrolyte is expected after the first aquation reaction. Conductivity data, therefore, indicates that the first aquation proceeds very slowly. No rate data were obtained for the aquation of *trans*-$[Cr([15]aneN_4)Cl_2]Cl\cdot 2H_2O$.

Discussion

An associative mechanism is consistent with most of our rate data. The ratio of rates of aquation for *cis*-$[Co(cyclen)Cl_2]Cl$ to *cis*-$[Co(cyclam)Cl_2]Cl$[2] is 0.26 to 1, while the ratio for *cis*-$[Cr(cyclen)Cl_2]Cl\cdot H_2O$ to *cis*-$[Cr(cyclam)Cl_2]Cl$[4] is 3040 to 1. These differences between the rates of Co(III) and Cr(III) aquations suggest that these two reactions are not proceeding by the same mechanism. A mechanism in which bond breaking is more important than bond formation (D mechanism) has been suggested for the aquation reactions of the cobalt(III) complexes, while a mechanism in which bond formation is more important than bond breakage (A mechanism) is believed to be more important for the aquation reactions of chromium(III) complexes.[3]

If cyclen is a weaker field ligand than cyclam as indicated by spectroscopic data,[5] and imposes more strain on a metal ion than cyclam as suggested by molecular models, then the cyclen should be less able to effectively donate electron density to the chromium(III) ion than the stronger field ligand, cyclam. As a consequence chromium(III) bonded to cyclen should have more electrophilic character than a chromium(III) bonded to cyclam. Therefore, if these reactions proceed by an A mechanism, *cis*-$[Cr(cyclen)Cl_2]^+$ should be more reactive toward water than *cis*-$[Cr(cyclam)Cl_2]^+$. However, if these reactions proceeded by a D mechanism, we would expect *cis*-$[Cr(cyclen)Cl_2]^+$ to be less reactive toward water than *cis*-$[Cr(cyclam)Cl_2]^+$. The fact that *cis*-$[Cr(cyclen)Cl_2]^+$ aquates faster than *cis*-$[Cr(cyclam)Cl_2]^+$ is consistent with an A mechanism.

The reasons for the facile aquations of *cis*-$[Cr(cyclen)Cl_2]^+$ and *trans*-$[Cr(isocyclam)Cl_2]^+$ require analysis. We have been assuming that *cis*-$[Cr(cyclen)Cl_2]^+$ is a more strained ion than the other cis complexes used in this study; and as a result of this additional strain energy, *cis*-$[Cr(cyclen)Cl_2]^+$ should be more susceptible to nucleophilic substitution. This assumes that a similar relationship exists between bond strain and the rates of aquation of these $[CrN_4Cl_2]^+$ complexes and the $[CoN_4Cl_2]^+$ complexes.[2] On the basis of this analogy, we would have to conclude from the rate data that *cis*-$[Cr(cyclen)Cl_2]^+$ is the most strained ion while *cis*-$[Cr(cyclam)Cl_2]^+$ is the least strained ion. It would also appear from the rate data that the isocyclam in *trans*-$[Cr(isocyclam)Cl_2]Cl$ imposes more strain on the chromium(III) than either the cyclam or the $[15]aneN_4$ in the analogous trans complexes. The rate of aquation of *trans*-$[Cr(isocyclam)Cl_2]Cl$ is approximately 4×10^7 times faster than that of *trans*-$[Cr(cyclam)Cl_2]Cl$,[4] while the rate of aquation of the *trans*-$[Cr([15]aneN_4)Cl_2]Cl\cdot 2H_2O$ is very slow and was not measured. The assumption that the same sequence of strain imposed by various macrocycles on chromium(III) is similar to that observed with cobalt(III) is based on spectral data for these chromium(III) compounds, which indicate that cyclen is a weaker field ligand than cyclam and that cyclam is a stronger field ligand than isocyclam. However, we are aware that there need not be a correlation between the ligand-field strength of a macrocycle and the bond strain that a ligand imposes on a given metal ion.

Although it is tempting to make similar conclusions for chromium(III) aquation reactions based on studies of analogous cobalt(III) complexes, such comparisons may be inappropriate. There are many aspects of chromium(III) chemistry that differ from those of cobalt(III) chemistry. For example, the ring size of the chelating ligand bonded to cobalt(III) influences the rate of aquation. However, the ring size of the chelating ligand does not affect the rate of aquation of analogous chromium(III) complexes.[9] Also, chromium(III) complexes are believed to be less stereomobile than analogous cobalt(III) complexes having similar nonrigid polydentate ligands.[10] Finally, the conformation of the macrocycle bonded to chromium(III) and cobalt(III) may be different. Such differences in the conformation of the coordinated ligand should affect bond strength and bond strain. As a result factors other than strain energy must be considered.

The fact that the rate constant for the aquation of the less strained *cis*-β-$[Cr(2,2,2\text{-}tet)Cl_2]^+$ is greater than that of the *cis*-$[Cr(cyclen)Cl_2]^+$[11] illustrates the multitude of factors influencing the aquation rates of these chromium(III) complexes. The macrocycle, cyclen, has the same configuration around the chromium(III) in *cis*-$[Cr(cyclen)Cl_2]^+$ as the 2,2,2-tet has in *cis*-β-$[Cr(2,2,2\text{-}tet)Cl_2]^+$. Therefore, it would appear that the large rate constants observed for these two complexes might be due to the similar manner of chelation around the chromium(III) ion rather than to the strain imposed by the tetradentate ligand on the metal ion.

Steric effects are likely to be another factor responsible for the fast rate of aquation of *cis*-$[Cr(cyclen)Cl_2]^+$ compared to that of most of the other *cis*-$[CrN_4Cl_2]^+$ complexes. In A mechanisms

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steric factors commonly influence the rates of reactions. Therefore the faster rate of hydrolysis of *cis*-$[Cr(cyclen)Cl_2]^+$ compared to that of *cis*-$[Cr(isocyclam)Cl_2]^+$ or *cis*-$[Cr(cyclam)Cl_2]^+$ could be due to the fewer number of carbon atoms in cyclen compared with those in cyclam and isocyclam. The smaller coordinated macrocycle should allow a more facile water attack on the chromium(III) than the larger ring systems. However, most of the linear tetradentate ligands have fewer carbon atoms than cyclen. Also, coordinated linear tetradentates have more flexibility in allowing a water molecule into the coordination sphere of the chromium(III) by being better able to move the terminal amine groups than the more inflexible and cumbersome tetradentate macrocycle. Therefore, it would be expected that the cis complexes containing a linear tetradentate ligand should be more reactive than the cis complexes containing cyclen. Since the opposite is true, with the exception of *cis*-β-$[Cr(2,2,2\text{-tet})]^+$, a simple steric argument cannot explain the rapid rate of acid hydrolysis of *cis*-$[Cr(cyclen)Cl_2]^+$ compared to that of other *cis*-$[Cr(N_4)Cl_2]^+$ complexes where N_4 is a linear tetradentate ligand.

A more subtle steric factor that may be responsible for the relative rate constants for the chromium(III) complexes listed in Table II is the conformation of the sec-NH protons. The conformation of the sec-NH protons will influence the steric barrier to an incoming water molecule and will affect the bond strain. The conformation of the sec-NH protons has been shown to affect the rate of aquation of many chromium(III) complexes.[10,11] Also the chemical equivalence of the two cis or trans chlorides will depend on the conformation of sec-NH protons. For example, if three of the NH groups are on one side of the N_4Cr plane and the fourth NH group is on the other side of the N_4Cr plane, the two chlorides will not be in the same environment, and as a result, their susceptibility to acid hydrolysis will be different. Therefore, without knowledge of the conformation of the chelate rings in solution for all complexes, the rapid rate of aquation of *cis*-$[Cr(cyclen)Cl_2]^+$ cannot be unambiguously assigned to any one factor.

The differences in the rate constants for the *trans*-$[Cr(N_4)Cl_2]^+$ complexes cannot be attributed to differences in the strain of the nitrogen to chromium bonds. The rates of aquation of *trans*-$[Cr(N_4)Cl_2]^+$ complexes are considerably more sensitive to the nature of the macrocycle around the chromium(III) than are the cis isomers. *trans*-$[Cr(isocyclam)Cl_2]^+$ aquates so fast that stop-flow techniques were necessary to follow the reaction. In contrast, its isomer, *trans*-$[Cr(cyclam)Cl_2]^+$, aquated about 4×10^7 times slower than *trans*-$[Cr(isocyclam)Cl_2]^+$, and *trans*-$[Cr([15]aneN_4)Cl_2]^+$ also aquated very slowly. Although it has been shown that isocyclam is a weaker field ligand than cyclam, the coordinated isocyclam may be less rigidly bonded to chromium(III) than cyclam, and as a result, an incoming water molecule should find easier access to the chromium(III) ion. It is, therefore, unlikely that the large differences in the rate constants observed for the trans Cr(III) complexes containing these ligands are caused only by the small differences in ring strain. Since an associative mechanism is expected, steric hindrance by hydrogen atoms on the trans six-membered rings may be responsible for the inertness of *trans*-$[Cr(cyclam)Cl_2]^+$ and *trans*-$[Cr[15]\text{-}aneN_4)Cl_2]^+$ ions. The greater flexibility of the trans isocyclam may contribute to a less sterically hindered access by a water molecule than the cyclam.

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Registry No. *cis*-$[Cr(cyclen)Cl_2]^+$, 101009-52-3; *cis*-$[Cr(isocyclam)Cl_2]^+$, 101009-49-8; *cis*-$[Cr(cyclen)(H_2O)Cl]^{2+}$, 101009-50-1; *trans*-$[Cr(isocyclam)Cl_2]^+$, 101009-51-2.

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Kinetics and Mechanism of the Reactions of Sulfito Complexes in Aqueous Solution. Formation, Aquation, and Intramolecular Electron-Transfer Reactions of the *trans*-Aquo(sulfito-*O*)bis(ethylenediamine)cobalt(III) Ion[1a]

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The rates of the rapid biphasic reversible uptake of SO_2 by the title complex have been determined by the stopped-flow technique, over the ranges $4.75 < pH < 7.00$, $10 < t < 20$ °C, and $0.01 < [S_T] < 0.1$ M at $I = 1.00$ M ($NaClO_4$). The reaction was found to follow two consecutive second-order steps. The rate parameters at 10 °C for the second-order reactions of SO_2 with *trans*-$Co(en)_2(OH_2)(OH)^{2+}$ and *trans*-$Co(en)_2(OH)_2^+$ are, respectively, $k = (7.5 \pm 0.5) \times 10^7$ and $(2.2 \pm 0.3) \times 10^9$ M^{-1} s^{-1}; $\Delta H^* = 6.4 \pm 2$ and 7.6 ± 3 kcal mol^{-1}, and $\Delta S^* = -11 \pm 1.4$ and -54 ± 30 cal deg^{-1} mol^{-1}. The reaction of the resulting mono(sulfito) species with SO_2 to form the bis(sulfito) species gave a second-order rate constant with hydrogen ion dependence of the form $k/[SO_2] = a + b/[H^+]$, where $a = (4.6 \pm 0.5) \times 10^6$ s^{-1} M^{-1} and $b = (5.4 \pm 0.2)$ s^{-1} at 10 °C. The products obtained are shown by spectral studies to be the O-bonded bis(sulfito) complex, which in the unstable protonated form $Co(en)_2(OSO_2H)_2^+$ eliminates SO_2 in a biphasic reaction in which the pseudo-first-order rate constants are directly proportional to $[H^+]$ in the ranges $2.97 < pH < 5.6$ and $10 < t < 15$ °C at $I = 1.00$ M ($NaClO_4$) with rate constants of $(2.4 \pm 0.4) \times 10^6$ and $(2.89 \pm 0.06) \times 10^3$ M^{-1} s^{-1} at 10 °C; $\Delta H^* = 11$ and 14 kcal mol^{-1} and $\Delta S^* = 25$ and 27 cal deg^{-1} mol^{-1}. The O-bonded bis(sulfito) intermediate undergoes reduction to Co(II) in the ranges $2.14 < pH < 5.5$ and $0.02 < [S_T] < 0.08$ M at $I = 1.0$ M ($NaClO_4$) at 25 °C, with a complicated hydrogen ion dependence. At pH = 5.5 and 25 °C, the pseudo-first-order rate constant for this relatively slow process is $(2.1 \pm 0.1) \times 10^{-3}$ s^{-1}. At pH >6, the sulfito-*O* intermediate rearranges to its sulfur-bonded analogue.

Introduction

The fast reversible uptake of SO_2 by octahedral hydroxo–metal complexes is well documented in the literautre[2-5] and occurs without metal–oxygen bond fission, as confirmed by oxygen-17 NMR measurements of the SO_2 uptake and elimination reactions

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(1) (a) A preliminary report of this work was presented at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983. See Abstract INOR 292. (b) Present address: Department of Chemistry, King Abdulaziz University, Jeddah, Saudi Arabia. (c) State University of New York at Buffalo.

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