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Quantitative Estimates of Steric Effects: Intramolecular Strain Energy Effects on the Activation Energy for Aquation of some *trans*-Dichlorotetraaminecobalt(III) Complexes*

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Abstract

In an effort to quantitatively estimate steric contributions to the aquation rates of a series of structurally related cobalt(III) tetraamine complexes, strain energy minimization calculations have been performed on the reactant and some plausible transition state structures. Free energies of activation $\Delta G^*_{\mathrm{obs}}$, are factored as:

$$\Delta G^*_{\mathrm{obs}} = \Delta G^*_{\mathrm{bb}} + \Delta G^*_{\mathrm{strain}} + \Delta G^*_{\mathrm{CF}} + \Delta G^*_{\mathrm{solvation}} + \ldots$$

where ΔG^*_{bb} is the free energy change associated with bond breaking, $\Delta G^*_{\mathrm{solvation}}$ is the solvation free energy difference between the reactant and a proposed transition state, ΔG^*_{CF} is the difference in crystal field stabilization between the reactant and a proposed transition state, and $\Delta G^*_{\mathrm{strain}}$ is the strain energy difference between the reactant complex and a proposed transition state. The activation energy for the aquation of a hypothetical 'strain free' complex is defined as $\Delta G^*_{\mathrm{int}}$ and reflects the energy required for the bond breaking step with all other terms. For the cations *trans*-(*RR*,*SS*)-dichloro-1,8-diamino-3,6-diazaoctanecobalt(III)(*trans* [Co(2,2,2-tet)Cl_2]$^+$), *trans*-(RR,SS)- or *trans*-(*RS*)-dichloro-1.9-diamino-3,7-diazanonanecobalt(III)(*trans* [Co(2,3,2-tet)Cl_2]$^+$ and *trans*-(*RS*)-dichloro-1,10-diamino-4,7-diazadecanecobalt(III)(*trans* [Co(3,2,3-tet)Cl_2]$^+$) $\Delta G^*_{\mathrm{int}}$ is found to be a constant 123 kJ/mol. For the *trans*-dichlorocobalt(III) complexes with the ligands 1,4,7,10-tetraazacyclotridecane([13]-ane-N_4), 1,4,8,11-tetraazacyclotetradecane([14]-ane-N_4), 1,4,8,12-tetraazacyclopentadecane([15]-ane-N_4) and 1,5,9,13-tetraazacyclohexadecane([16]-ane-N_4), $\Delta G^*_{\mathrm{int}}$ lies in the range 133–139 kJ/mol.

Introduction

The relationship between structure, reactivity and strain energy has long been recognized, but has generally been difficult to quantify [2]. The concepts of ring strain and steric hinderance have been used to explain the stereochemical course of both organic and inorganic reactions (distribution of products) and in a qualitative way to explain major differences in reactivity. Steric arguments have been used so often that they have gained a reputation as a 'catch all' term to explain differences in reactivity which cannot be attributed to well defined properties of the reactants and products.

The application of conformational analysis to problems in coordination chemistry dates back to the classic paper by Corey and Bailar in which the conformational energies of diamine chelates were estimated [3]. Over the last 15 years conformational analysis (strain energy minimization) calculations has been applied to increasingly diverse problems in coordination stereochemistry [4]. The vast majority of these studies have been structural in nature; calculating energy minimized structures for a series of cobalt(III) complexes with amine ligands [5]. More recently, molecular mechanics has been applied to complexes with other metal ions and different donor atoms [6]. Still the vast majority of the studies have been concerned with the energy minimized structure of a complex.

A few studies, however, have focussed upon the use of the strain energy to explain patterns in the stability of a series of complexes [6, 7]. These studies, while often limited in scope have successfully explained the stability of the various members of a series of copper(II) complexes with macrocycle ligands [6]. A recent study has shown a relationship between the stability of complexes with various metals and the 'hole size' of a macrocyclic ligand [8]. Another study has used molecular mechanics

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to estimate the Franck-Condon barrier to electron transfer [9]. This increased use of the strain energy minimized structures suggests that molecular mechanics might be used to model actual inorganic reactions.

The substitution reactions of many six coordinate transition metal complexes appear to proceed through a dissociative (D) mechanism in acidic medium. In a dissociative process [10], the first and rate limiting step is the loss of a ligand to produce a very short lived [11] five coordinate species. Either simultaneous with the loss of the ligand, or within a few vibrational periods (10^{-9} s), this species relates to either a trigonal pyramidal or square pyramidal intermediate which subsequently reacts with a nucleophile to complete the coordination sphere.

The complex cation (*trans*-dichloro-1,8-diamino-3,6-diazaoctane cobalt(III)(*trans*$[Co(2,2,2\text{-tet})Cl_2]^+$ was studied thoroughly by Buckingham, Sargeson and their students [12] and others [13]. In contrast with bis(diamine) and macrocyclic ligand systems and with the longer chain tetraamine ligand systems *trans*-$[Co(2,2,2\text{-tet})Cl_2]^+$ is a minor product [14], presumably because of the strain introduced by the bridging ethylene link [15]. The aquation rate and activation parameters are very different from those of the simpler diamine complexes as, of course, is the distribution of products [15, 16].

Aquation reactions of *trans*-dichloro cobalt(III) complexes with the tetraamine ligand 1,9-diamino-3,7-diazanonane (2,3,2-tet) have been studied by Hamilton and Alexander [17] and by Tobe and his coworkers [18]. *trans* Isomers are dominant in the coordination chemistry of 2,3,2-tet and higher homologs. The two *trans* complexes of this ligand differ only in the relative configuration of the two secondary nitrogen donors and, therefore, in one isomer, the six membered chelate ring must adopt a skew boat arrangement [19]. Aquation of *trans*-(RR,SS)-$[Co(2,3,2\text{-tet})Cl_2]^+$ produces a mixture of uns-*cis* and *trans*-$[Co(2,3,2\text{-tet})(H_2O)Cl]^{2+}$ while the aquation of *trans*-(RS)-$[Co(2,3,2\text{-tet})Cl_2]^+$ produces only *trans*-(RS)-$[Co(2,3,2\text{-tet})(H_2O)Cl]^{2+}$ [17, 18].

Busch and his students [20] and several other workers [21, 22] have carefully characterized numerous complexes of cobalt(III) with macrocyclic tetraamine ligands. These studies include syntheses of most of the isomers of cobalt(III) with this homologous series of ligands. For one series of *trans*-dichloro-tetraazamacrocycle complexes, electronic and PMR spectra have been measured, and aquation rates and activation parameters have been measured and correlated with ring size [20, 23, 24].

In this report, we will discuss the use of strain energy minimization calculations to estimate steric contributions through a model of a dissociative reaction.

Methods

Molecular Mechanics

Strain energy minimization calculations were performed using the calculation scheme described previously [25].

Initial Coordinates

Trial coordinates for the 2,3,2-tet and 3,2,3-tet complexes were derived from published crystal structures [26]. Trial coordinates for [16]-ane-N_4 structures were derived from the energy minimized coordinates for the open chain tetraamine ligands. Initial coordinates for the lower homologs were derived from the energy minimized [16]-ane-N_4 structure by systematic deletion of methylene groups.

Interaction Constants

The interaction constants used for the known complexes in this study have been published elsewhere [27]. We have assumed that the metal-donor bond deformation force constants, and non-bonded interaction constants involving the metal ion are unchanged in the transition state and reactant structures. This assumption is supported by the observation that metal nitrogen stretching frequencies are relatively insensitive to changes in charge on the metal complex [28]. Additional support may be derived from the vibrational force constants for cobalt(III) and cobalt(II). The cobalt(II)–N force constant is only 40% smaller than the cobalt(III)–N force constant and these are much smaller than the C–C and C–N force constants which yield the majority of the bond deformation strain energies [29].

Angle deformation constants and unstrained angles around the metal center of the proposed transition state are not well defined, and were replaced by the non-bonded repulsions between the donor atoms. Hambley *et al.* [30] have shown that although absolute energies obtained from this modified force field differ from those obtained using the standard Urey-Bradley force field (UBFF), energies can be compared within either model. Accordingly, the original structures and all of the transition states for each complex were calculated using the Hambley and Hawkins modification to the UBFF.

Structures and energies were calculated for two different possible transition states. The first transition state is calculated by simply deleting one chlorine atom and its associated interactions from the input file. A large damping factor was applied to permit calculation of the strain energy of this species without allowing the coordinates to shift. The second possible transition state is calculated by allowing the structure obtained in the first transition state to relax under the influence of the force field until a converged structure is obtained (r.m.s. coordinate shift of 1 pm). At this point all non-bonded interactions less than or equal to 300 pm were included in the force field. The structures of these transition states normally required between three and six iterations to converge.

Results

Flexible Tetraamine Complexes

The calculated structure of *trans*-[Co(2,2,2-tet)-Cl_2]$^+$ is highly strained (strain energies are tabulated in Table I) due to the stereochemical requirements of three coplanar five membered chelate rings. The strain energy of the *trans* complex is substantially higher than is found for similar complexes with other coordination geometries [31, 32]. The structure of the first postulated transition state retains the high strain energy (Table II), suggesting that the primary source of strain is the angle deformations required by the metal ion in a *trans* coordination geometry. A substantial release of strain occurs when a chloride is released and the complex is allowed to relax to the strain equilibrated transition state (Table III). This accounts for the rapid aquation rate of this complex in aqueous acid along with the low activation barrier for the reaction. The structure of the strain equilibrated transition state also shows a substantial change in geometry (Fig. 1) which suggests that the product of the reaction should not be the *trans* isomer consistent with the experimental observations [11].

TABLE I. Ground State Strain Energies for some Cobalt(III) Dichloro Tetraamine Complexes

Ligand	Strain energy (kJ/mol)
2,2,2-tet	62
RS-2,3,2-tet	48
RR,SS-2,3,2-tet	62
[13]-ane-N_4	95
[14]-ane-N_4	72
[15]-ane-N_4(I)[a]	121
[15]-ane-N_4(II)[a]	128
[16]-ane-N_4	198

[a] (I) and (II) refer to the two different isomers of *trans*-[Co-([15]-ane-N_4)Cl_2]$^+$ which have been prepared.

TABLE II. Strain Energies for the First[a] Plausible Transition State for some Cobalt(III) Dichloro Tetraamine Complexes

Ligand	Strain energy (kJ/mol)
2,2,2-tet	51
RS-2,3,2-tet	45(51)[b]
RR,SS-2,3,2-tet	54
[13]-ane-N_4	78(77)[b]
[14]-ane-N_4	58
[15]-ane-N_4(I)	103(116)[b]
[15]-ane-N_4(II)	114
[16]-ane-N_4	186

[a] The first plausible transition state arises from the removal of one chlorine atom and all of the associated interactions from the input deck and calculation of the strain energy without allowing the atoms to move. [b] The numbers in parentheses indicate the strain energy calculated when the other chlorine atom is removed in cases where there are two nonequivalent chlorines.

TABLE III. Strain Energies for the Second[a] Plausible Transition State for some Cobalt(III) Dichloro Tetraamine Complexes

Ligand	Strain energy (kJ/mol)
2,2,2-tet	25
RS-2,3,2-tet	25(31)[b]
RR,SS-2,3,2-tet	32
[13]-ane-N_4	51(49)[b]
[14]-ane-N_4	39
[15]-ane-N_4(I)	77(92)[b]
[15]-ane-N_4(II)	86
[16]-ane-N_4	156

[a] The second plausible transition state arises from the removal of one chlorine atom and all of the associated interactions from the input deck and calculation of the strain energy allowing the atoms to move in order to release strain. [b] The numbers in parentheses indicate the strain energy calculated when the other chlorine atom is removed in cases where there are two nonequivalent chlorines.

The calculated structure of *trans*-(*RS*)-[Co(2,3,2-tet)Cl_2]$^+$ shows the three chelate rings in the conformations normally expected for chelate rings of their size. The six-membered chelate ring is in a slightly flattened chair conformation with nearly 'normal' bond distances but greater than normal bond angles around the carbon and nitrogen atoms (Fig. 2a). The five membered chelate rings are in the staggered conformation with regular bond distances and angles around both the carbon and nitrogen atoms. The structure of this complex is qualitatively and quantitatively similar to the experimentally determined structure of [Cu(2,3,2-tet)$(ClO_4)_2$] [26a]. The principal differences between the cobalt(III) and copper(II) structures are the replacement of chloride for perchlorate, and cobalt for copper with the expected slightly smaller metal donor bond distances in the cobalt(III) complex.

The calculated structure of the optically active isomer *trans*-(*RR,SS*)-[Co(2,3,2-tet)Cl_2]$^+$ is much higher in strain energy than *trans*-(*RS*)-[Co(2,3,2-

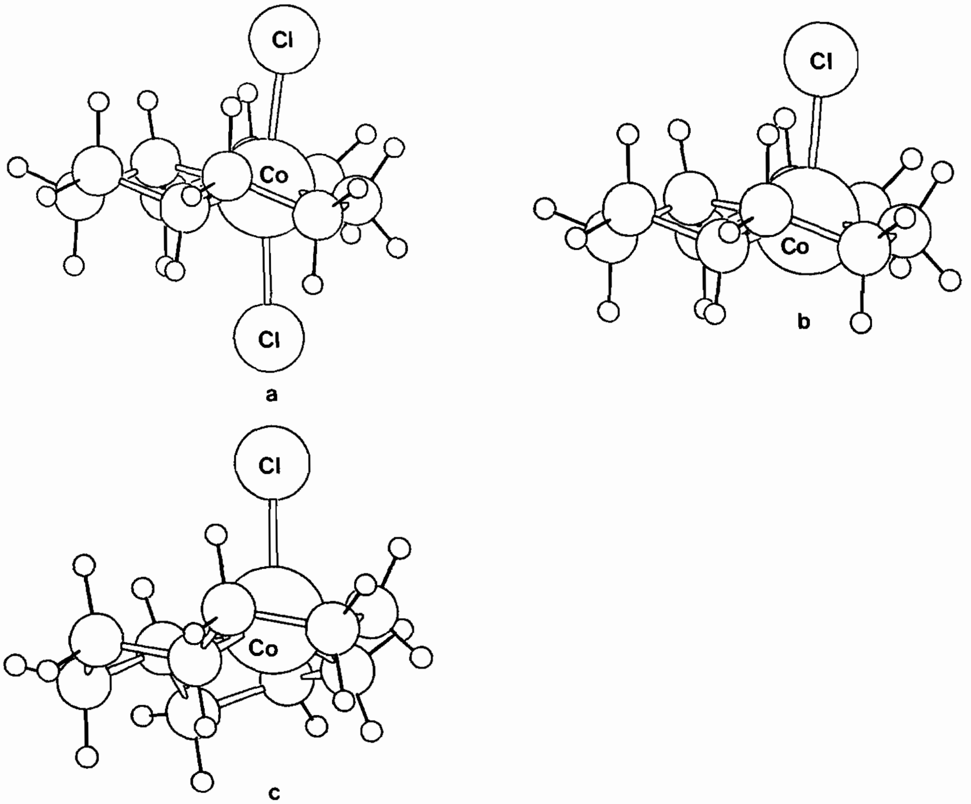

Fig. 1. Calculated structures for *trans*-[Co(2,2,2-tet)Cl$_2$]$^+$ and associated transition states. (a) The original complex; (b) transition state 1; (c) transition state 2 (see text for explanation of different transition states).

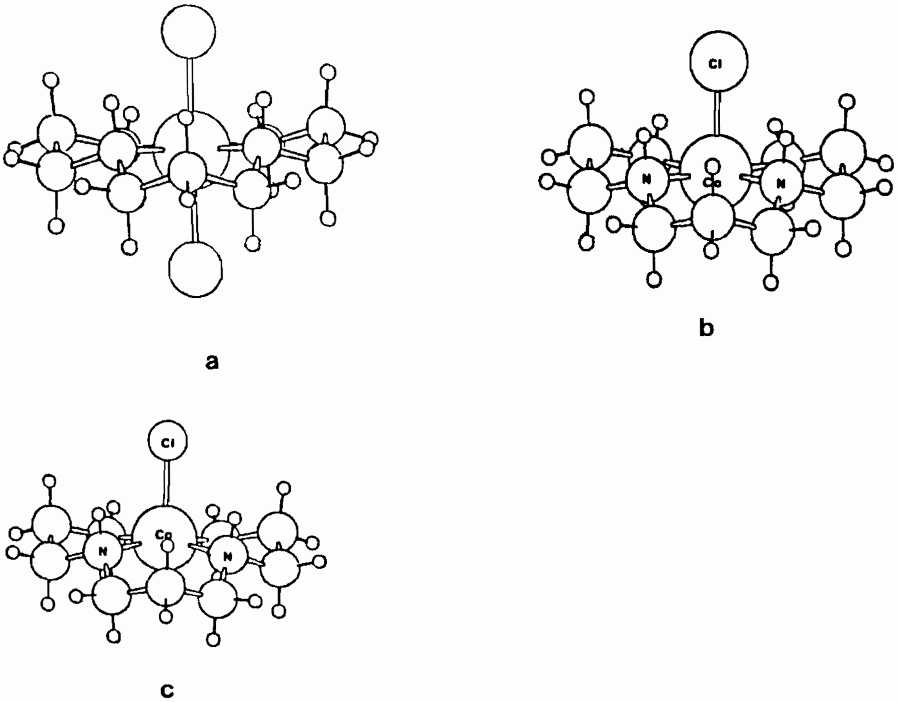

Fig. 2. Calculated structures for *trans*-(*RS*)-[Co(2,3,2-tet)Cl$_2$]$^+$ and associated transition states. (a) The original complex: (b) transition state 1; (c) transition state 2 (see text for explanation of different transition states).

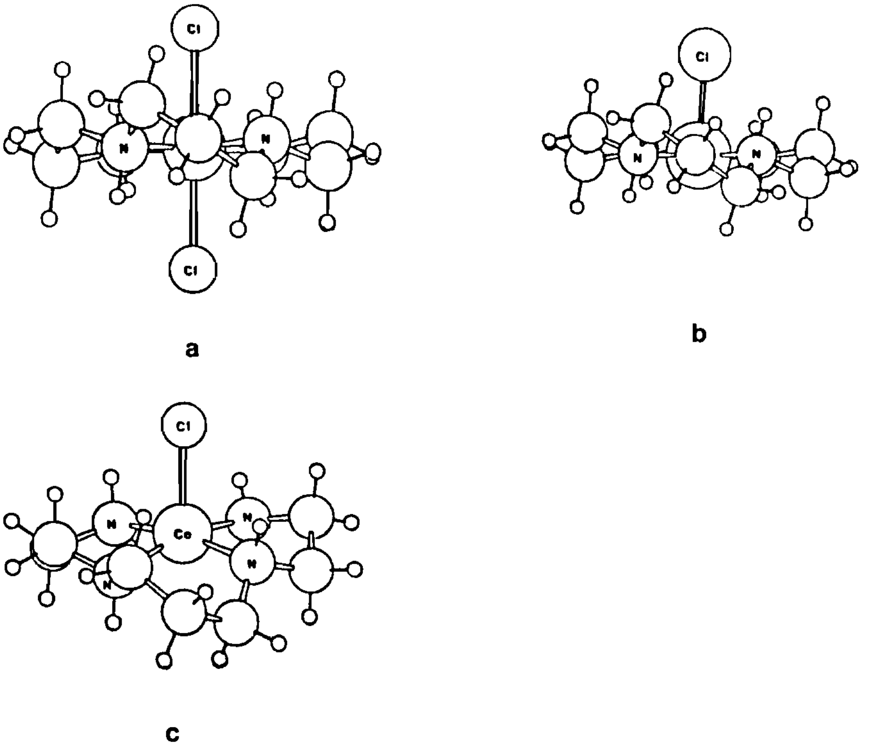

Fig. 3. Calculated structures for *trans*-(*RR*,*SS*)-[Co(2,3,2-tet)Cl_2]$^+$ and associated transition states. (a) The original complex; (b) transition state 1; (c) transition state 2 (see text for explanation of different transition states).

tet)Cl_2]$^+$ (the calculated strain energies are given in Table I). The major reason for the higher strain energy is the adoption of a skew-boat conformation by the six-membered chelate ring (Fig. 3a) consistent with the proton and carbon-13 NMR spectra [33]. In this chelate ring conformation, the principal contributors to the increased energy are the torsional angle deformations and the non-bonded interactions. The five-membered chelate rings remain in the staggered conformation with 'normal' bond distances and bond angles.

In the structure of the strain equilibrated transition state (*RS*)-[Co(2,3,2-tet)Cl]$^{2+}$, the nitrogen-chlorine and proton chlorine non-bonded interaction distances are lengthened to achieve a square pyramidal structure with the cobalt atom above the plane of the four nitrogen donors (Fig. 2c). As in the calculated ground state structures, the non-bonded interactions involving the protons bound to the secondary amine donors are the most significant contributors to the strain energy.

The structure of the strain equilibrated transition state derived from the optically active (*RR*,*SS*)-[Co(2,3,2-tet)Cl_2]$^+$ complex shows a 'folding under' (Fig. 3c) of the six membered chelate ring caused by relaxation of some valence and torsional angle deformations and the decrease of some non-bonded interactions.

Tetraazamacrocycle Complexes

Structures have not been reported for all of the tetraazamacrocycle complexes in this study. The bond distances and angles in our strain energy minimized structure lie within 1 pm and 2°, respectively, of the distances and angles determined experimentally for the complex [Co([14]-ane-N_4)(ClO_4)$_2$]$^+$ [34]. Thus, starting with coordinates estimated from other complexes, we calculate a cobalt(III)–N distance of 199 pm which may be compared with 198 pm found in the crystal and 213 pm calculated using an earlier force field model [23, 24]. Similarly, we find C–N and C–C distances which deviate from the crystal structure by about 1 pm, or about the r.m.s. coordinate shift in our final cycle of refinement. Our Co–N–C bond angles of 108° and 118° and N–Co–N angles of 88° and 91° in the five and six membered chelate rings, respectively, may be compared with the crystallographic angles of 108°, 118°, 85° and 94°. We find no unusual bond distances or angles and conclude that, within our convergence criteria and the precision of the results we wish to correlate, all of these structures have converged to consistent molecular geometries and strain energies.

Strain energy minimized structures of five coordinate monochlorotetraazamacrocycle cobalt(III) complexes (Fig. 4) generally conform to the transition

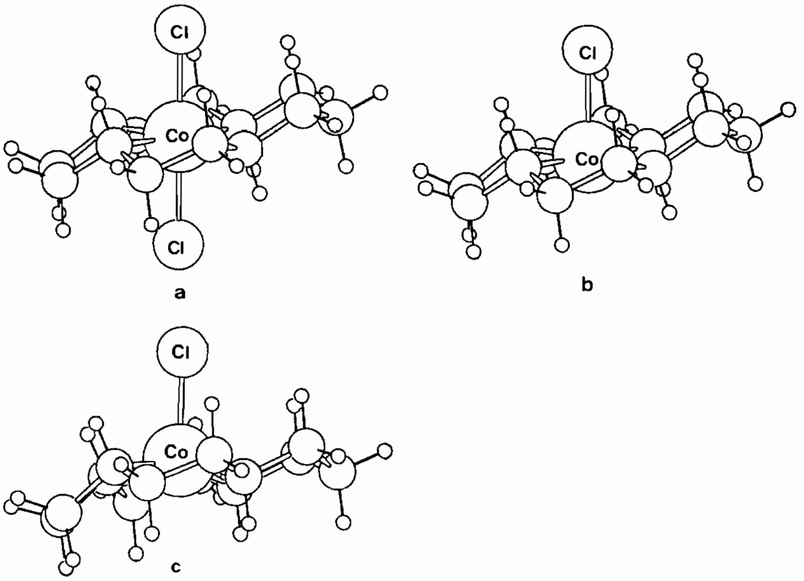

Fig. 4. Calculated structures for *trans*-[Co([13]-aneN$_4$)Cl$_2$]$^+$ and associated transition states. (a) The original complex; (b) transition state 1; (c) transition state 2 (see text for explanation of different transition states).

state proposed by Busch [24], with the metal ion displaced from the mean plane of the four nitrogen donors in the direction of the remaining chloride. The details of these structures depend on the conformations of the chelate rings as well as on the number of atoms in the macrocycle.

Intramolecular strain energies are summarized in Table I. The strain energies we find for the tetraazamacrocycle complexes are somewhat higher than those reported by Busch and his students [23, 24], largely because we have employed slightly different force field parameters. It is particularly important to note that strain energy is not a simple monotonic function of the number of atoms or interactions in the calculation. That is, strain energy is a minimum for the [14]-ane-N$_4$ complex and greater for both the [13]-ane-N$_4$ and [15]-ane-N$_4$ complexes.

In *trans*-(*RS*)-[Co(2,3,2-tet)Cl$_2$]$^+$, *trans*-[Co([13]-ane-N$_4$)Cl$_2$]$^+$ and *trans*-[Co([15]-ane-N$_4$)Cl$_2$]$^+$ (isomer I), there are two nonequivalent chlorides. Our strain energy minimization calculations indicate a preferential loss of one chloride (Tables I–III). This selectivity arises primarily from non-bonded repulsions between the coordinated chlorine atom and the protons bound to the secondary amine nitrogens.

Discussion

The Activation Energy of the Reaction

The experimentally determined activation parameters for the aquation of these *trans*-dichloro cobalt(III) complexes in aqueous acid are measurably different (Table IV). We consider the activation enthalpy of the reaction to be comprised of several terms.

TABLE IV. Experimental Activation Parameters for the Aquation of some Cobalt(III) Dichloro Tetraamine Complexes

Ligand	ΔH^*	ΔS^*	ΔG^*	Reference
2,2,2-tet	110	+59	93	12c
RS-2,3,2-tet	102	+4	101	18
RR,SS-2,3,2-tet	108	+50	93	18
[13]-ane-N$_4$	107	+53	91	24b
[14]-ane-N$_4$	103	−13	107	24b
[15]-ane-N$_4$(I)	82	−31	91	24b
[15]-ane-N$_4$(II)	66	−61	84	24b

$$\Delta H^*_{obs} = \Delta H^*_{bb} + \Delta H^*_{strain} + \Delta H^*_{CF} + \Delta H^*_{solvation} + \ldots$$

where ΔH^*_{bb} is the enthalpy involved in bond breaking, $\Delta H^*_{solvation}$ is the solvation energy difference between the reactant and the transition state, ΔH^*_{CF} is the difference in crystal field stabilization between the reactant and the transition state and ΔH^*_{strain} is the strain energy difference between the reactant and a postulated transition state. We have summarized ΔH^*_{strain} calculated under previously stated assumptions in Tables I–III. A 'strain free' enthalpy of activation may be calculated, for the dissociation of a chloride to give each of the proposed transition states.

$$\Delta H^*_{sf} = \Delta H^*_{obs} - \Delta H^*_{strain}$$

The values of ΔH^*_{sf} are not constant with this series of complexes.

Solvation effects in this series of complexes are somewhat more difficult to quantify. The dielectric continuum model for an ionic species in a polar solvent allows the solvation energy to be readily understood [35]. In this model, the solvation energy is related to the size and charge of the solvated ion. The energy of this type of solvent interaction varies systematically throughout the various series of complexes. We are unable to account for differences in the experimental activation parameters using this model.

For low spin cobalt(III) complexes, a 4 *Dq* loss of crystal field stabilization energy accompanies the loss of one chloride to form the transition state. In the vibrationally equilibrated transition state, crystal field stabilization is expected to favor the square pyramidal transition state over the trigonal bipyramidal transition state by 7.48 *Dq* [10]. In the cases of chloropentaamine complexes of cobalt(III) there is loss of only 2 *Dq* in crystal field stabilization in going from a six coordinate complex to a square pyramidal five coordinate complex. Since these *trans*-dichloro species are among the most completely characterized tetragonal complexes, crystal field parameters have been resolved into *xy* and *z* components [22, 23, 26]; Dq_{xy} lies in the range 32.9–27.5 kJ/mol and Dq_z lies in the range 16.1–18.1 kJ/mol ([13]-ane-N_4 first and [15]-ane-N_4 in each case). With the exception of the two isomers of the [15]-ane-N_4 complex, crystal field parameters vary monotonically with the number of methylene groups, suggesting that there is an exceptional crystal field contribution to the activation energy only in this case.

The strain free enthalpy of activation is combined with the experimental entropies of activation to yield the 'strain free' activation free energy

$$\Delta G^*_{int} = \Delta H^*_{sf} - T\Delta S^*$$

Calculation of the strain free activation free energy yields the activation energy for the release of chloride from a hypothetical 'strain free' *trans*-dichlorotetraamine cobalt(III) complex to arrive at a 'strain free' transition state. The values of this parameter should therefore be independent of the stereochemistry of the complex.

The observed values for ΔG^*_{int} for the strain equilibrated transition states (Table V) lie in two groups within the errors associated with the measurements and the calculations. A comparison of the values of ΔG^*_{int} for the two groups, and the complexes associated with the groups is instructive. For the complexes derived from open chain tetraamines, *trans*-(*RR*,*SS*)-dichloro-1,8-diamino-3,6-diazaoctanecobalt(III)(*trans*[Co(2,2,2-tet)Cl_2]$^+$, *trans*-(*RR*,*SS*)- or *trans*-(*RS*)-dichloro-1,9-diamino-3,7-diazanonanecobalt(III)(*trans*[Co(2,3,2-tet)Cl_2]$^+$) and *trans*-(*RS*)-dichloro-1,10-diamino-4,7-diazadecane cobalt(III)(*trans*[Co(3,2,3-tet)Cl_2]$^+$) ΔG^*_{int} is found to be a constant 123 kJ/mol. For the complexes derived from the macrocyclic ligands 1,4,7,10-tetraazacyclotridecane([13]-ane-N_4), 1,4,8,11-tetraazacyclotetradecane([14]-ane-N_4), 1,4,8,12-tetraazacyclopentadecane([15]-ane-N_4) and 1,5,9,13-tetraazacyclohexadecane([16]-ane-N_4), ΔG^*_{int} lies in the range 133–139 kJ/mol. Comparison of ΔG^*_{int} values at other places along the reaction coordinate (e.g. the transition state derived from deletion of the chlorine atom without allowing relaxation) (Table VI) does not lead to a constant value.

TABLE V. Intrinsic Free Energies of Activation for some Cobalt(III) Dichloro Tetraamine Complexes Using the Second Plausible Transition State[a]

Ligand	ΔG^*_{int}
2,2,2-tet	126
RS-2,3,2-tet	123
RR,*SS*-2,3,2-tet	123
[13]-ane-N_4	137
[14]-ane-N_4	139
[15]-ane-N_4(I)	135
[15]-ane-N_4(II)	127

[a] The second plausible transition state arises from the removal of one chlorine atom and all of the associated interactions from the input deck and calculation of the strain energy allowing the atoms to move in order to release some of the ring strain.

TABLE VI. Intrinsic Free Energies of Activation for some Cobalt(III) Dichloro Tetraamine Complexes Using the First Plausible Transition State[a]

Ligand	ΔG^*_{int}
2,2,2-tet	100
RS-2,3,2-tet	104
RR,*SS*-2,3,2-tet	102
[13]-ane-N_4	109
[14]-ane-N_4	121
[15]-ane-N_4(I)	109
[15]-ane-N_4(II)	98

[a] The first plausible transition state arises from the removal of one chlorine atom and all of the associated interactions from the input deck and calculation of the strain energy without allowing the atoms to move.

The Stereochemical Course of the Reaction

The difference in the products of the aquation of the two *trans* complexes of [Co(2,3,2-tet)Cl_2]$^+$

suggests that the stereochemistry of the products is a direct result of the structure of the strain equilibrated transition state [15]. The energy minimized transition state formed from the dissociation of a chloride ion from *trans*-(*RS*)-[Co(2,3,2-tet)Cl_2]$^+$ (Fig. 2c) has only one area where an entering nucleophile (in this case water) can approach the metal ion without encountering unreasonable non-bonded repulsions. Approach along this pathway leads directly to the *trans* aquation product. Approaches which would lead to the *cis* product appear to be much higher in strain energy for approach to the metal ion. The difference in strain energy between the two possible reaction paths, suggests that a single aquation product is formed, consistent with experimental observation.

The strain equilibrated transition state derived from the model for the aquation of *trans*-(*RR,SS*)-[Co(2,3,2-tet)Cl_2]$^+$ shows a 'folding under' (Fig. 3c) of the six membered chelate ring caused by the relaxation of some of the valence and torsional angle deformations and the decrease of some non-bonded interactions. This folding under provides an avenue for *cis* attack of the entering nucleophile and partially obscures the axis of *trans* attack. Thus either a *trans* or an uns-*cis* may be formed from this transition state. Approach of the nucleophile from below and perpendicular to the plane of the nitrogen donors leads to the formation of the *trans* aquation product. Approach of the nucleophile from the front and above the plane of the nitrogen donors leads to the formation of the uns-*cis* isomers. The relative sizes of the free volumes along the two avenues of attack suggest, qualitatively a 50:50 mixture of the two aquation products should be formed. Experimentally, Tobe [18] found a 50 ± 20% retention of the geometry of the product. A quantitative estimate of the stereochemical conversion is beyond the scope of this work.

The strain equilibrated transition state structures for the remaining complexes in this study show some release of valence and torsion angle deformations. This release of strain arises from the formation of square pyramidal structures with the cobalt(III) ion above the plane formed by the four nitrogen donors. In none of these complexes is there significant obstruction of the *trans* axis of attack, leading only to the formation of *trans* aquation products. This observation is consistent with the experimental observation of only a single product.

Conclusions

This work illustrates the use of molecular mechanics calculations to model reactions of coordination complexes. The results of the study show that the release of strain energy is an important portion of the experimentally observed free energy of activation. The primary portions of the enthalpy of activation appear to be the bond breaking, and strain energy.

It is observed that when the enthalpy of activation, after removal of the strain component, is combined with the experimental entropy of activation to calculate an intrinsic free energy of activation (ΔG^*_{int}), a constant value is obtained for the open chain tetraamine ligands, and a second constant value is obtained for the macrocycle complexes. The difference between these two constants remains unexplained.

The observation that only the energies associated with the strain equilibrated transition state lead to a constant value of ΔG^*_{int} suggests that the dissociation of the chloride ion is accompanied by the relaxation of the structure. The transition state associated with simple removal of the chloride ion does not lead to a constant ΔG^*_{int}, which implies that this state is never actually formed, but that the loss of the chloride ion is assisted by the release of strain energy.

It is also observed that the products of a reaction may be determined for the structures of the transition state. This observation suggests that molecular mechanics may be used to model the stereochemical course of a reaction. It is anticipated that the reactions of many other species, along with a variety of other reaction mechanisms may be modelled with molecular mechanics calculations.

Acknowledgements

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