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Mechanism and Stereochemistry of the Water Exchange Reactions on Aqua Amine Complexes of Chromium(III): The Role of the "Spectator" Ligands

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The water exchange reactions on $Cr(NH_3)_5OH_2^{3+}$, $Cr(NH_2CH_3)_5OH_2^{3+}$, *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$, *trans*-$Cr(NH_3)_4(NH_2CH_3)OH_2^{3+}$, $Ru(OH_2)_6^{3+}$, and $Cr(OH_2)_6^{3+}$ (the latter having been reinvestigated with an improved model) have been studied with ab initio quantum chemical calculations on the hydrated ions, whereby the solvent was treated as a dielectric continuum. The computations on $Ru(OH_2)_6^{3+}$ have been performed because of similarities in the electronic structures of the transition states [*cis*-$Cr(OH_2)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ and [*cis*-$Ru(OH_2)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$. The water exchange reaction on $Cr(NH_2CH_3)_5OH_2^{3+}$ proceeds with a dissociative activation, which is due to the bulky NH_2CH_3 ligands. As in the analogous case of Rh^{III}, the calculations did not allow the distinction of the dissociative interchange (I_d) from the dissociative (D) mechanism. All of the other reactions follow the associative interchange (I_a) mechanism with retention of the configuration. The M$\cdots$O bond lengths in the transition states for this interchange mechanism increase with increasing basicity of the "spectator" ligands, whereas the effect of the ligand trans to the exchanging H_2O molecules is much larger than that of the cis ligands. The increase of the M$\cdots$O bond lengths is paralleled by a corresponding variation of the experimental activation volumes. Finally, the calculations showed that putative square pyramidal pentacoordinated intermediates, for example $Cr(NH_3)_5^{3+}$ and $Cr(NH_2CH_3)_5^{3+}$, exhibit activation energies for the rearrangement via a trigonal bipyramidal transition state that are considerably higher than those found for water addition. The situation is similar for Ru^{III}, and the activation energy for the corresponding process of Rh^{III} is higher. Thus, all thermally activated substitution reactions on Cr^{III}, Ru^{III}, and Rh^{III} proceed with retention of the configuration.

Introduction

The mechanism of ligand exchange reactions, which represent the most simple type of substitution processes, is attributed on the basis of thermodynamic activation parameters such as the activation enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) or volume ($\Delta V^{\ddagger}$). The latter is defined by eq 1, whereby *k* is the rate constant of the reaction, *P* is the pressure, *T* is the temperature, and *R* is the gas constant.

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \tag{1}$$

The experimental activation volume ($\Delta V^{\ddagger}$) is considered as the sum of an intrinsic ($\Delta V_{int}^{\ddagger}$) and electrostrictive ($\Delta V_{el}^{\ddagger}$) component (eq 2).[1]

$$\Delta V^{\ddagger} = \Delta V_{int}^{\ddagger} + \Delta V_{el}^{\ddagger} \tag{2}$$

$\Delta V_{int}^{\ddagger}$ arises from the changes in the metal–ligand bond lengths, bond breaking or bond making processes, whereas $\Delta V_{el}^{\ddagger}$ is due to the electrostriction of the solvent caused by the creation or annihilation of charge or dipoles during the activation process.[1]

The attribution of exchange mechanisms should be based on $\Delta V_{int}^{\ddagger}$ but, because this parameter is not available experimentally, one has to resort to $\Delta V^{\ddagger}$. In exchange processes involving neutral ligands, $\Delta V_{el}^{\ddagger}$ is expected to be small or constant for similar reactions of similar reactants. In such cases, the changes in $\Delta V^{\ddagger}$ reflect the corresponding changes in $\Delta V_{int}^{\ddagger}$.

Positive activation volumes suggest a dissociative (D) or dissociative interchange (I_d) mechanism, negative activation volumes suggest an associative (A) or associative interchange (I_a) mechanism, and values close to zero suggest the interchange (I) mechanism. The D and A mechanisms proceed via a penta- and a heptacoordinated intermediate, respectively, whereas the interchange mechanisms (I_d, I, and I_a) do not involve any intermediate.

Quantum chemical calculations of all of the stationary points (reactants/products, transition states, and intermediates, if there are any) on the potential energy surface of such an exchange reaction yield activation energies ($\Delta E^{\ddagger}$)[2] and the exchange mechanism, which can be attributed on the basis of the structure and the imaginary mode of the transition state.[3,4] Furthermore, the computations supply the $\Delta\Sigma d(M{-}L)$ parameter (eq 3), which represents the change of the sum of all M–L bond lengths for the transformation of the reactant into the transition state. (L denotes all atoms that are or will be bound to the metal center (M) in the activation process; the summation is made over 6 M–L bonds for the D mechanism, and for the others, it is made over 7 M–L bonds.)

$$\Delta\Sigma d(M{-}L) = \Sigma d(M{-}L)_{transition\ state} - \Sigma d(M{-}L)_{reactant} \tag{3}$$

For the water exchange reaction on first-row transition metal hexaaqua ions, it has been shown[3,4] that the *sign* of $\Delta\Sigma d(M{-}L)$ is equal to that of $\Delta V^{\ddagger}$. For the similar reactants and reactions, investigated in the present study, the magnitude of $\Delta V_{int}^{\ddagger}$ is also likely to be proportional to $\Delta\Sigma d(M{-}L)$.

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Ligand substitution reactions on a variety of amine complexes of chromium(III), all exhibiting quartet electronic ground states, have been and still are studied extensively in order to understand their reaction mechanisms. In particular, the activation volumes ($\Delta V^{\ddagger}$) of complexes with neutral leaving and entering groups were investigated[5−8] because the electrostrictive component ($\Delta V_{el}^{\ddagger}$) was believed to be approximately constant within such a series of compounds. These activation volumes span the wide range of -2.0 to -10.8 cm^3/mol and depend on the leaving groups and on the nature of the ligands that are not substituted. The latter, denoted in the following as L_s, will be called “spectator” ligands. The negative activation volumes suggest the I_a mechanism for all these substitution reactions.[5−7]

The present quantum chemical calculations on water exchange reactions of aqua amine and hexaaqua complexes of Cr^{III} and Ru^{III} were performed for obtaining a deeper insight into the substitution mechanisms of pseudo-octahedral complexes of Cr^{III}. In this study, the role of the spectator ligands (L_s), the origin of the appreciable variation in $\Delta V^{\ddagger}$, and the stereochemical course of the exchange reactions (which has not yet been studied experimentally for such compounds) were systematically analyzed. The relationship between structural features of the transition states and $\Delta V^{\ddagger}$ is discussed.

The role of the electronic structure of the metal center and that of bulky ligands on the exchange or substitution mechanism is rationalized. It is shown why the reactivity of high-spin d^3 complexes of Cr^{III} is similar to that of low-spin d^5 complexes of Ru^{III}. The substitutional reactivity of Cr^{III} is also compared with that of the low-spin d^6 systems of Rh^{III} and Co^{III}, and the origin of their disparate reactivity is explained.

All stationary points on the potential energy surface of the water exchange reactions[5,7] of $Cr(NH_3)_5OH_2^{3+}$ and $Cr(NH_2CH_3)_5OH_2^{3+}$ (eqs 4 and 5) have been computed for interchange (I_a or I_d) and the dissociative (D) pathways as described[9,10] for $Ru(NH_3)_5OH_2^{3+}$, $Rh(NH_3)_5OH_2^{3+}$, and $Rh(NH_2CH_3)_5OH_2^{3+}$.

$$Cr(NH_3)_5OH_2^{3+} + \mathbf{H_2O} \rightarrow Cr(NH_3)_5\mathbf{OH_2}^{3+} + H_2O \qquad (4)$$

$$Cr(NH_2CH_3)_5OH_2^{3+} + \mathbf{H_2O} \rightarrow Cr(NH_2CH_3)_5\mathbf{OH_2}^{3+} + H_2O \qquad (5)$$

To explore the role of the basicity and the steric effects of the spectator ligands, L_s, the water exchange reaction on $Cr(OH_2)_6^{3+}$ (eq 6), which has already been calculated[4] on the basis of a gas-phase model, has been reinvestigated by taking into account the hydration and electron correlation using the improved model[9] which has been applied[11] to the corresponding reactions of $V(OH_2)_6^{2+}$, $Mn(OH_2)_6^{2+}$, and $Fe(OH_2)_6^{2+}$.

$$Cr(OH_2)_6^{3+} + \mathbf{H_2O} \rightarrow Cr(OH_2)_5\mathbf{OH_2}^{3+} + H_2O \qquad (6)$$

The water exchange reaction on $Ru(OH_2)_6^{3+}$ (eq 7) via the I_a pathway has been computed in order to expose the origin of the similarities between the high-spin Cr^{III} and the low-spin Ru^{III} centers. The comparison was made for the water exchange reactions on the corresponding hexaaqua and aqua pentaammine ions.

$$Ru(OH_2)_6^{3+} + \mathbf{H_2O} \rightarrow Ru(OH_2)_5\mathbf{OH_2}^{3+} + H_2O \qquad (7)$$

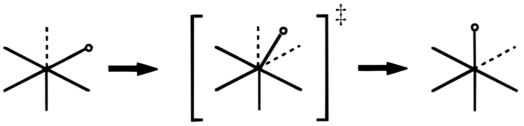
The pressure and temperature dependence of reactions 4−7 have been measured,[5,7,12−14] and the activation parameters, in particular $\Delta V^{\ddagger}$ and $\Delta H^{\ddagger}$, are therefore available. This allows for the comparison of the computational results with experimental data. To systematically explore the role of the spectator ligands on $\Delta V_{int}^{\ddagger}$, exchange reactions 8 and 9, for which no activation parameters are available, have been calculated as well.

$$trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+} + \mathbf{H_2O} \rightarrow trans\text{-}Cr(NH_3)_4(OH_2)(\mathbf{OH_2})^{3+} + H_2O \qquad (8)$$

$$trans\text{-}Cr(NH_3)_4(NH_2CH_3)OH_2^{3+} + \mathbf{H_2O} \rightarrow trans\text{-}Cr(NH_3)_4(NH_2CH_3)\mathbf{OH_2}^{3+} + H_2O \qquad (9)$$

The structural data on reactions 4−9 allow the determination of the cis and trans effect as well as the role of the steric and electronic effects on $\Delta V_{int}^{\ddagger}$; the latter are related to the basicity of L_s.

For the elucidation of the stereochemistry of the water exchange reaction proceeding via the D mechanism, the activation energies for the rearrangement (eq 10) of the square pyramidal pentacoordinated intermediates $Cr(NH_3)_5^{3+}$ and $Cr(NH_2CH_3)_5^{3+}$ have been calculated, and the rearrangement of the corresponding complexes of Ru^{III} and Rh^{III} is discussed.



(10)

Results

The model, its approximations, limitations, and the computational procedures have been described in previous studies.[3,4,9−11] The geometry optimizations and the computations of the energy were performed for the hydrated ions, whereby the surrounding solvent was treated as a dielectric continuum. The total energies and changes of the sum of all M−L bond lengths, $\Delta\Sigma d(M-L)$ (eq 3), for all species involved in reactions 4−10 are reported in Table 1, and the corresponding M−N and M−O bond lengths are given in Table 2 (M = Cr^{III} and Ru^{III}). For the large $Cr(NH_2CH_3)_5$ systems, two basis sets have been used for the geometry optimizations as for the corresponding Rh^{III} complexes.[10]

In the following sections, the computational results of the water exchange reactions on $Cr(NH_3)_5OH_2^{3+}$, $Cr(NH_2CH_3)_5OH_2^{3+}$, $Cr(OH_2)_6^{3+}$, $Ru(OH_2)_6^{3+}$, *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$, and *trans*-$Cr(NH_3)_4(NH_2CH_3)OH_2^{3+}$ (eqs 4−9) are described. The last section treats the rearrangement of the square pyramidal pentacoordinated intermediates $Cr(NH_3)_5^{3+}$ and $Cr(NH_2CH_3)_5^{3+}$ (eq 10).

Reactions of $Cr(NH_3)_5OH_2^{3+}$ (eq 4). As in the studies of the water exchange on the aqua pentaamine complexes of Ru^{III} and Rh^{III},[9,10] two interchange pathways and the dissociative mechanism (D) have been investigated. In the first interchange pathway, the entering water attacks adjacent to the aqua ligand, and in the second pathway, the entering water attacks opposite to the aqua ligand. Thus, the first pathway leads to retention of the configuration, and the second one to stereomobility. The D pathway proceeds via a pentacoordinated intermediate, whose rearrangement (eq 10) via a trigonal bipyramidal transition state is described in the last section.

The activation energy ($\Delta E^{\ddagger}$),[2] computed for the interchange pathway with retention of the configuration, is the lowest one and agrees with experiment (Table 1). The negative $\Delta\Sigma d(Cr-L)$ (eq 3) value indicates that $\Delta V_{int}^{\ddagger}$ is negative and therefore, the attribution of the I_a mechanism to reaction 4 is straightforward. The stereomobile interchange pathway is the least favorable one, because its activation energy is higher by more than 30 kJ/mol.

TABLE 1: Calculated Total and Relative Energies, Experimental Activation Parameters, and Change of the Sum of the Metal−Ligand Bond Lengths

species	basis set	E[a] (hartrees)	$\Delta E^\ddagger$ or ΔE (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta\Sigma d(M-L)$ (Å)	$\Delta V^\ddagger$ (cm^3/mol)
$Cr(NH_3)_5OH_2{\cdot}OH_2^{3+}$	A	−520.067 256 (24)	0.0		0.0	
[*cis*-$Cr(NH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$	A	−520.026 783 (392)	106.3	97.1 ± 2.1[b]	−0.57	−5.8 ± 0.2[b]
$[Cr(NH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$ [c]	A	−520.014 388 (392)	138.8		−0.10	
$Cr(NH_3)_5OH_2^{3+}$	A	−443.833 448 (1)	0.0		0.0	
$[Cr(NH_3)_5{\cdots}OH_2^{3+}]^\ddagger$	A	−443.788 343 (24)	118.4		1.25	
$Cr(NH_3)_5{\cdot}OH_2^{3+}$	A	−443.788 338 (392)	118.4		1.70	
$Cr(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$	B	−715.528 656 (24)	0.0		0.0	
[*cis*-$Cr(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$	B	−715.479 975 (392)	127.8	98.5 ± 3[d]	0.33	−3.8 ± 0.3[d]
$Cr(NH_2CH_3)_5OH_2^{3+}$	B	−639.294 752 (392)	0.0		0.0	
$[Cr(NH_2CH_3)_5{\cdots}OH_2^{3+}]^\ddagger$	B	−639.256 108 (392)	101.5	98.5 ± 3[d]	1.26	−3.8 ± 0.3[d]
$Cr(NH_2CH_3)_5{\cdot}OH_2^{3+}$	B	−639.256 161 (392)	101.3		1.71	
$Cr(OH_2)_6{\cdot}OH_2^{3+}$	A	−619.234 894 (1)	0.0		0.0	
[*cis*-$Cr(OH_2)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$	A	−619.198 227 (1)	96.3	108.6 ± 2.7[e]	−0.98	−9.6 ± 0.1[e]
$Ru(OH_2)_6{\cdot}OH_2^{3+}$	A	−626.437 429 (75)	0.0		0.0	
[*cis*-$Ru(OH_2)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$	A	−626.402 447 (75)	91.8	89.8 ± 4[f]	−0.97	−8.3 ± 2.1[f]
trans-$Cr(NH_3)_4(OH_2)_2{\cdot}OH_2^{3+}$	A	−539.898 838 (1)	0.0		0.0	
$[Cr(NH_3)_4OH_2{\cdots}(OH_2)_2^{3+}]^\ddagger$ [g]	A	−539.856 943 (24)	110.0		−0.92	
trans-$Cr(NH_3)_4(NH_2CH_3)OH_2{\cdot}OH_2^{3+}$	A	−559.218 015 (392)	0.0		0.0	
$[Cr(NH_3)_4NH_2CH_3{\cdots}(OH_2)_2^{3+}]^\ddagger$ [h]	A	−559.175 288 (392)	112.2		−0.36	
$Cr(NH_3)_5^{3+}$, SQP	A	−367.561 402 (392)	0.0		0.0	
$[Cr(NH_3)_5^{3+}]^\ddagger$, TBP	A	−367.553 296 (392)	21.3		0.04	
$[Cr(NH_3)_5^{3+}]^\ddagger$, TBP[i]	A	−367.472 264 (784)	234.0			
$[Cr(NH_3)_5^{3+}]^\ddagger$, TBP[j]	A	−367.473 850 (784)	229.9		0.01	
$Cr(NH_2CH_3)_5^{3+}$, SQP	B	−563.027 656 (392)	0.0		0.0	
$[Cr(NH_2CH_3)_5^{3+}]^\ddagger$, TBP	B	−563.019 239 (392)	22.1		0.04	

[a] In parentheses: number of configuration state functions of the CAS−SCF wave function. [b] Reference 5. [c] Attack opposite to the leaving H_2O ligand. [d] Reference 7. [e] References 12 and 13. [f] Reference 14. [g] The two exchanging water ligands are cis to each other, and the aqua ligand is trans to the exchanging water molecules. [h] The two exchanging water ligands are cis to each other, and the methylamine ligand is trans to the exchanging water molecules. [i] Doublet electronic state, at the geometry of the quartet state. [j] Doublet electronic state, geometry optimized for the doublet state.

The activation energy for the dissociative mechanism is intermediary, and this pathway is also unlikely to operate for reaction 4, especially because of its positive $\Delta\Sigma d(Cr-L)$ value, which is inconsistent with the negative experimental[5] activation volume (Table 1). The attribution of reaction mechanisms should be made on the basis of $\Delta G^\ddagger$ and not $\Delta H^\ddagger$, but the present model,[11] in which the second coordination sphere is not treated quantum chemically, does not allow the computation of $\Delta S^\ddagger$ and, therefore, $\Delta G^\ddagger$ also. In this case, the mechanism of reaction 4 can be attributed on the basis of the calculated $\Delta E^\ddagger$ and $\Delta\Sigma d(Cr-L)$ parameters. It is interesting to note that the corresponding pentacoordinated intermediate $Cr(NH_3)_5{\cdot}OH_2^{3+}$ has, on the basis of the present model and its limitations, the same energy as the transition state $[Cr(NH_3)_5{\cdots}OH_2^{3+}]^\ddagger$. Therefore, the lifetime of the pentacoordinated intermediate would be extremely short.

Reactions of $Cr(NH_2CH_3)_5OH_2^{3+}$ (eq 5). Because the stereomobile interchange pathway was the least favorable one, for the water exchange reaction of $Cr(NH_3)_5OH_2^{3+}$, it has not been investigated for this large system.

The computed activation energy for the interchange pathway with retention of the configuration is 128 kJ/mol (Table 1), higher than the experimental[7] $\Delta H^\ddagger$ value by 29 kJ/mol. For the analogous reaction of Rh^{III}, the calculated[10] $\Delta E^\ddagger$ value was too low by 22 kJ/mol. It is striking that the average Cr···O bond lengths (3.32 Å, Table 2) in the transition state [*cis*-$Cr(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$ (Figure 1) are close to those of the corresponding Rh^{III} species,[10] and especially that they are considerably longer (by 0.52 Å) than those in [*cis*-$Cr(NH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$ (Figure 2). Otherwise, these two structures are quite similar.

The calculated activation energy for the dissociative mechanism agrees with experiment (Table 1). Since the $\Delta E^\ddagger$ values for both the I$_d$ and the D pathways were too low, by 22 kJ/mol, for the analogous reaction of Rh^{III} , the present agreement should not be taken as sound evidence for the D pathway or as a safe argument against the I$_d$ mechanism. Possible reasons for these deviations have been discussed,[10] and these criteria are also valid for reaction 5. The negative experimental activation volume[7] argues against the D mechanism, unless the electrostrictive component is quite negative, and this cannot be excluded for the present methylamine complexes. Alternatively, the negative $\Delta V^\ddagger$ value could arise from a small positive intrinsic activation volume, which would be compatible with the small and positive $\Delta\Sigma d(Cr-L)$ parameter for the I$_d$ mechanism (Table 2) and a moderately negative electrostrictive component. As already mentioned, because of the unavailability[11] of $\Delta S^\ddagger$ and $\Delta G^\ddagger$ in the present model, it is not always possible to attribute substitution mechanisms unambiguously on the basis of such computations. To summarize, $\Delta E^\ddagger$ favors the D mechanism and $\Delta\Sigma d(Cr-L)$ the I$_d$ pathway. The present model does not allow the distinction of these two mechanisms, but the computational data permit the conclusion that reaction 5 proceeds with a dissociative activation. Because the energy of the pentacoordinated intermediate $Cr(NH_2CH_3)_5{\cdot}OH_2^{3+}$ is very close to that of the transition state $[Cr(NH_2CH_3)_5{\cdots}OH_2^{3+}]^\ddagger$, this intermediate would have an extremely short lifetime.

Reactions of $Cr(OH_2)_6^{3+}$ (eq 6). The associative interchange (I$_a$) and the dissociative (D) pathways have already been studied[4] on the basis of a gas-phase model.[3] The I$_a$ mechanism, which is followed by reaction 6, was reinvestigated by taking into account hydration and electron correlation, and the pertinent data is given in Tables 1 and 2. As for the hexaaqua ions[11] of V^{II}, Mn^{II}, and Fe^{II}, the inclusion of hydration effects did not lead to significant alterations of the geometries. Also, the calculated activation energy remained the same, but it should be noted that the present calculation was based on a different reactant structure (in which the water molecule in the second coordination sphere is hydrogen bonded to two aqua ligands in a bridging mode),[11] and this is the reason, why the present value of $\Delta\Sigma d(Cr-L)$ is lower than that based on the gas-phase model

TABLE 2: Metal−Ligand Bond Lengths and Change of Their Sum during the Activation[a]

	L_s						
species	d(Cr−N)	d(Cr−O)	d(Cr−O)	Σd(Cr−L_s)	Σd(Cr−L)	ΔΣd(Cr−L_s)	ΔΣd(Cr−L)
(i) basis set A:							
$Cr(NH_3)_5OH_2{\cdot}OH_2^{3+}$	2.159, 2.164, 2.157, 2.164, 2.170		2.061, 4.026	10.814	16.901	0.0	0.0
$[\textit{cis}\text{-}Cr(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$	2.149, 2.150, 2.133, 2.146, 2.149		2.811, 2.794	10.727	16.332	−0.087	−0.569
$[Cr(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ [b]	2.190, 2.146, 2.136, 2.108[c]		3.055[c]	10.688	16.798	−0.126	−0.103
$Cr(NH_3)_5OH_2^{3+}$	2.160, 2.169, 2.167, 2.160, 2.154		2.104	10.810	12.914	0.0	0.0
$[Cr(NH_3)_5{\cdots}OH_2^{3+}]^{\ddagger}$	2.125,[c] 2.148,[c] 2.101		3.512	10.647	14.159	−0.163	1.245
$Cr(NH_3)_5{\cdot}OH_2^{3+}$	2.132,[c] 2.146,[c] 2.105		3.954	10.661	14.615	−0.149	1.701
$Cr(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$	2.180, 2.165, 2.158 2.187, 2.171		2.076, 4.042	10.861	16.979	0.0	0.0
$[\textit{cis}\text{-}Cr(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$	2.130, 2.132, 2.109, 2.142, 2.162		3.280, 3.364	10.675	17.319	−0.186	0.340
$Cr(NH_2CH_3)_5OH_2^{3+}$	2.170, 2.179, 2.151, 2.168, 2.175		2.126	10.843	12.969	0.0	0.0
$[Cr(NH_2CH_3)_5{\cdots}OH_2^{3+}]^{\ddagger}$	2.139, 2.127, 2.100, 2.145, 2.161		3.552	10.672	14.224	−0.171	1.255
$Cr(NH_2CH_3)_5{\cdot}OH_2^{3+}$	2.140, 2.137, 2.100, 2.143, 2.159		3.997	10.679	14.676	−0.164	1.707
$Cr(OH_2)_6{\cdot}OH_2^{3+}$		2.048, 2.044,[c] 2.041, 2.015	2.022, 3.824	10.192	16.038	0.0	0.0
$[\textit{cis}\text{-}Cr(OH_2)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$		2.045,[c] 2.062,[c] 2.053	2.397[c]	10.267	15.061	0.075	−0.977
$Ru(OH_2)_6{\cdot}OH_2^{3+}$		2.124, 2.089, 2.088,[c] 2.136	2.084, 3.825	10.525	16.434	0.0	0.0
$[\textit{cis}\text{-}Ru(OH_2)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$		2.129,[c] 2.127,[c] 2.089	2.433[c]	10.601	15.467	−0.076	−0.967
$\textit{trans}\text{-}Cr(NH_3)_4(OH_2)_2{\cdot}OH_2^{3+}$	2.158, 2.159,[c] 2.149	2.083	2.041, 4.008	10.708	16.757	0.0	0.0
$[Cr(NH_3)_4OH_2{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ [d]	2.160,[c] 2.148[c]	2.089	2.565[c]	10.705	15.835	−0.003	−0.922
$\textit{trans}\text{-}Cr(NH_3)_4(NH_2CH_3)OH_2{\cdot}OH_2^{3+}$	2.170, 2.158, 2.154, 2.173, 2.162		2.064, 4.007	10.817	16.888	0.0	0.0
$[Cr(NH_3)_4NH_2CH_3{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ [e]	2.141, 2.146, 2.142, 2.148, 2.120[f]		2.921, 2.907	10.697	16.525	−0.120	−0.363
$Cr(NH_3)_5^{3+}$, SQP	2.144, 2.101,[g] 2.146, 2.145, 2.146				10.682		0.0
$[Cr(NH_3)_5^{3+}]^{\ddagger}$, TBP	2.116, 2.117, 2.139 2.139, 2.206				10.717		0.035
$[Cr(NH_3)_5^{3+}]^{\ddagger}$, TBP[h]	2.123, 2.125, 2.137, 2.137, 2.170				10.692		0.010
$Cr(NH_2CH_3)_5^{3+}$, SQP	2.155, 2.152, 2.096,[g] 2.136, 2.154				10.693		0.0
$[Cr(NH_2CH_3)_5^{3+}]^{\ddagger}$, TBP	2.114, 2.153, 2.126, 2.136, 2.200				10.729		0.036
(ii) Basis set B:							
$Cr(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$	2.176, 2.162, 2.154, 2.183, 2.168		2.078, 4.049	10.843	16.970	0.0	0.0
$[\textit{cis}\text{-}Cr(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$	2.128, 2.130, 2.105, 2.140, 2.160		3.278, 3.357	10.663	17.298	−0.180	0.328
$Cr(NH_2CH_3)_5OH_2^{3+}$	2.167, 2.175, 2.148, 2.164, 2.172		2.129,	10.826	12.955	0.0	0.0
$[Cr(NH_2CH_3)_5{\cdots}OH_2^{3+}]^{\ddagger}$	2.137, 2.125, 2.097, 2.142, 2.158		3.555	10.659	14.214	−0.167	1.259
$Cr(NH_2CH_3)_5{\cdot}OH_2^{3+}$	2.138, 2.134, 2.097, 2.140, 2.156		3.997	10.665	14.662	−0.161	1.707
$Cr(NH_2CH_3)_5^{3+}$, SQP	2.152, 2.149, 2.093,[g] 2.133, 2.151				10.678		0.0
$[Cr(NH_2CH_3)_5^{3+}]^{\ddagger}$, TBP	2.111, 2.150, 2.124, 2.133, 2.196				10.714		0.036

[a] Units: angstroms. [b] Attack opposite to the leaving H_2O ligand. [c] Two symmetry equivalent bonds. [d] The two exchanging water ligands are cis to each other, and the aqua ligand is trans to the exchanging water molecules. [e] The two exchanging water ligands are cis to each other, and the methylamine ligand is trans to the exchanging water molecules. [f] **Cr**−**N**H_2CH_3 bond length. [g] Apical Cr−N bond. [h] Doublet electronic state.

(in which the water in the second coordination sphere forms a single hydrogen bond with an aqua ligand).

Among all presently discussed transition states for interchange mechanisms, these Cr···O bonds of 2.40 Å are the shortest (Table 2), and the cause of that is the weak trans effect of water (see the Discussion section).

Reaction of $Ru(OH_2)_6^{3+}$ (eq 7). At first glance, this reaction does not seem to have any relationship to those of Cr^{III}. Its I_a exchange pathway has been investigated because the common feature of the transition states $[\textit{cis}\text{-}Ru(OH_2)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ and $[\textit{cis}\text{-}Cr(OH_2)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ is that in both species one antibonding orbital of the d_{β} type[4,10,11] (Figure 3) is populated by a single

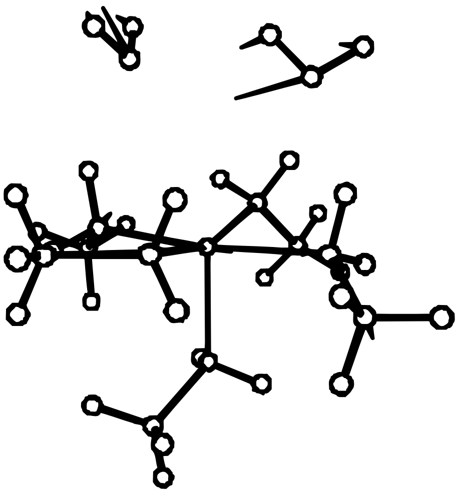


Figure 1. Perspective view and imaginary mode of the transition state [*cis*-$Cr(NH_2CH_3)_5 \cdots (OH_2)_2^{3+}]^{\ddagger}$ (I_d mechanism, attack adjacent to the leaving water ligand).

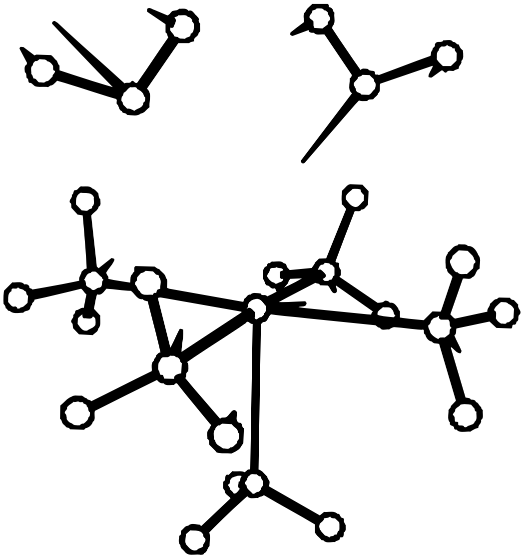


Figure 2. Perspective view and imaginary mode of the transition state [*cis*-$Cr(NH_3)_5 \cdots (OH_2)_2^{3+}]^{\ddagger}$ (I_a mechanism, attack adjacent to the leaving water ligand).

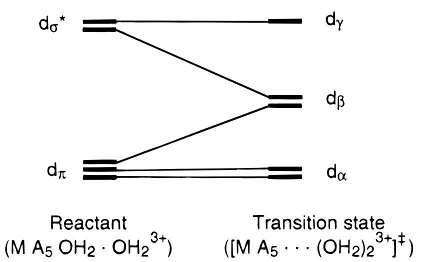


Figure 3. Qualitative orbital diagram of reactants/products $MA_5OH_2^{3+}$ and transition states $[MA_5 \cdots (OH_2)_2^{3+}]^{\ddagger}$.

electron. The d_α orbitals are nonbonding and occupied by 2 and 4 electrons in the transition states of Cr^{III} (which has a high-spin d^3 electron configuration) and Ru^{III} (which is a low-spin d^5 system), respectively. Therefore, the structures of these transition states were expected to be similar, and this is indeed the case because the corresponding Ru···O and Cr···O bond lengths are virtually equal and so are the corresponding ΔΣd(M−L) values (Table 2). Also for this exchange reaction, $\Delta E^{\ddagger}$ agrees with experiment. Furthermore, it should be noted that the experimental[12−14] activation volumes of reactions 6 and 7 are close.

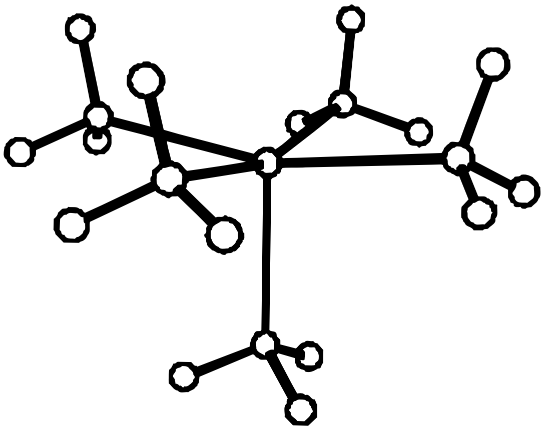


Figure 4. Perspective view of the square pyramidal pentacoordinated intermediate $Cr(NH_3)_5^{3+}$.

Reaction of *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ (eq 8). Its interchange pathway, proceeding with retention of the configuration, has been investigated for the analysis of the cis and trans effect via the comparison of the Cr···O bond lengths in the transition states. Like the species involved in reaction 6, the reactant has C_s and the transition state C_2 symmetry. The higher basicity of the (equatorial) ammonia ligands is responsible for the longer Cr···O bonds in the transition state $[Cr(NH_3)_4OH_2 \cdots (OH_2)_2^{3+}]^{\ddagger}$ compared with [*cis*-$Cr(OH_2)_5 \cdots (OH_2)_2^{3+}]^{\ddagger}$ (Table 2). The ΔΣd(Cr−L) value is similar to that of reaction 6. Because no experimental activation parameters are available, the accuracy of $\Delta E^{\ddagger}$ is unknown, but its error should not exceed 10 kJ/mol as in the other cases (Table 1).

Reaction of *trans*-$Cr(NH_3)_4(NH_2CH_3)OH_2^{3+}$ (eq 9). The reactant of this reaction was derived via the substitution of the trans NH_3 ligand in $Cr(NH_3)_5OH_2^{3+}$ by the more basic NH_2CH_3 ligand. The thus increased basicity is responsible for the elongation of the Cr···O bonds by 0.11 Å with respect to those in [*cis*-$Cr(NH_3)_5 \cdots (OH_2)_2^{3+}]^{\ddagger}$ (Table 2). Also for this reaction, the measured activation parameters are not available.

Stereomobility of the Square Pyramidal (SQP) Pentacoordinated Intermediate $Cr(NH_3)_5^{3+}$ (eq 10). It has C_1 symmetry (Figure 4) and was obtained by the computation of the intrinsic reaction coordinate starting from the trigonal bipyramidal (TBP) transition state $[Cr(NH_3)_5^{3+}]^{\ddagger}$ (vide infra). The total energy (of its quartet electronic ground state) and the Cr−N bond lengths are given Tables 1 and 2. The apical Cr−N bond is shorter than the equatorial ones by 0.044 Å. The two 3d orbitals of Cr^{III}, a singly occupied d_π level and an empty $d_\sigma{}^*$ level,[15] lying in the plane in which the rearrangement according to eq 10 takes place, are shown in Figure 5. The reduction of the N−Cr−N angle of 164.6° to 131.1° (in the plane of Figure 5) makes the singly occupied nonbonding orbital MO 31 (Figure 5 (a)) antibonding, whereas MO 33 remains unoccupied and antibonding. This is the reason that the trigonal bipyramidal (TBP) species, $[Cr(NH_3)_5^{3+}]^{\ddagger}$ (Figure 6), with a quartet electronic state, is a transition state. The two 3d orbitals in the trigonal plane are depicted in Figure 7. The singly occupied MO 31 of $Cr(NH_3)_5^{3+}$ (Figure 5 (a)) became antibonding in $[Cr(NH_3)_5^{3+}]^{\ddagger}$ (MO 32, Figure 7 (a)), and this the reason that the energy of this transition state is higher than that of the square pyramidal intermediate $Cr(NH_3)_5^{3+}$ (Table 1). The singly occupied antibonding MO 32 (Figure 7 (a)) is also the cause for the elongation of the Cr−N bond (2.21 Å, Table 2) of the rearranging NH_3 ligand.

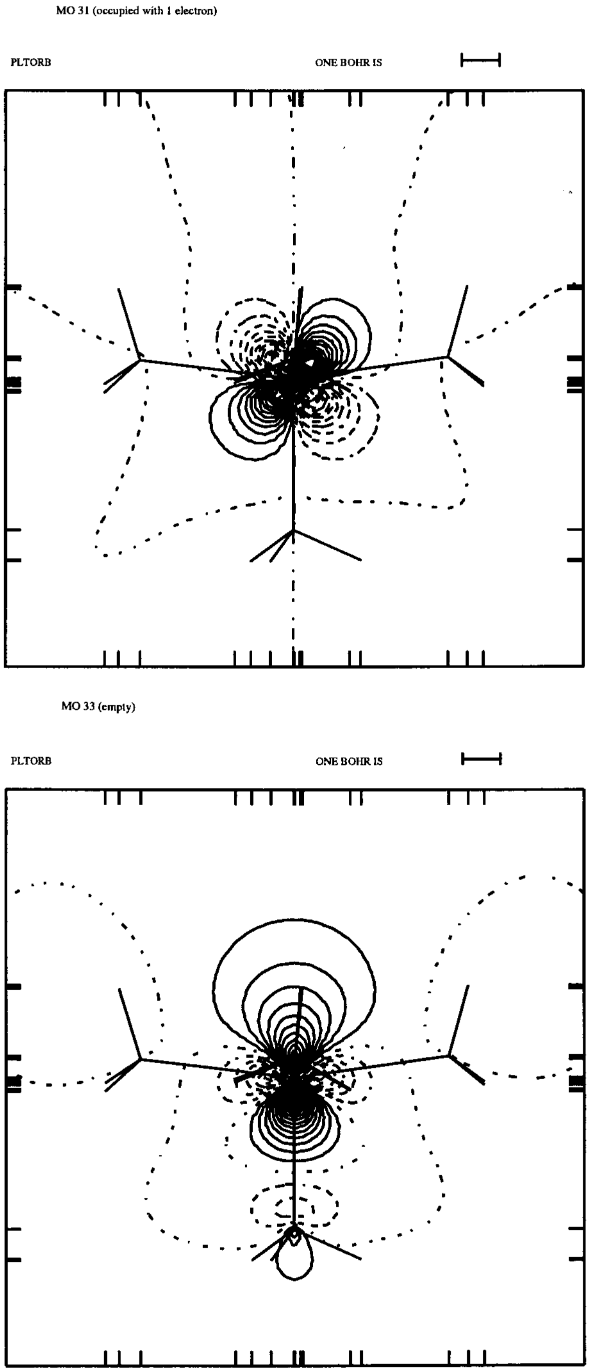


Figure 5. Contour plots depicting the 3d orbitals of $Cr(NH_3)_5^{3+}$ in the plane, in which one NH_3 ligand will move in the rearrangement according to eq 10: (a) singly occupied nonbonding d_π orbital, MO 31; (b) empty antibonding d_σ* orbital, MO 33.

In $[Cr(NH_3)_5^{3+}]^‡$, there is a singly occupied antibonding orbital, thus the energy of the lowest doublet electronic state has been calculated at the geometry of the quartet electronic state (Table 1), and it is higher by more than 200 kJ/mol. The optimization of the geometry of this doublet state lead to wee metrical changes, and its energy was not lowered significantly (Table 2). These computations demonstrate that doublet electronic states are irrelevant in the rearrangement of $Cr(NH_3)_5^{3+}$ according to eq 10.

Because of the high energy of the lowest doublet electronic state of $[Cr(NH_3)_5^{3+}]^‡$, only the lowest quartet states were considered in the computations on the rearrangement of $Cr(NH_2CH_3)_5^{3+}$. The activation energy (Table 1) is insignificantly different from that of the corresponding NH_3 complex. This shows, that the bulky NH_2CH_3 ligands do not facilitate the rearrangement according to eq 10 and therefore, there is no release of strain in the trigonal bipyramidal transition state $[Cr(NH_2CH_3)_5^{3+}]^‡$.

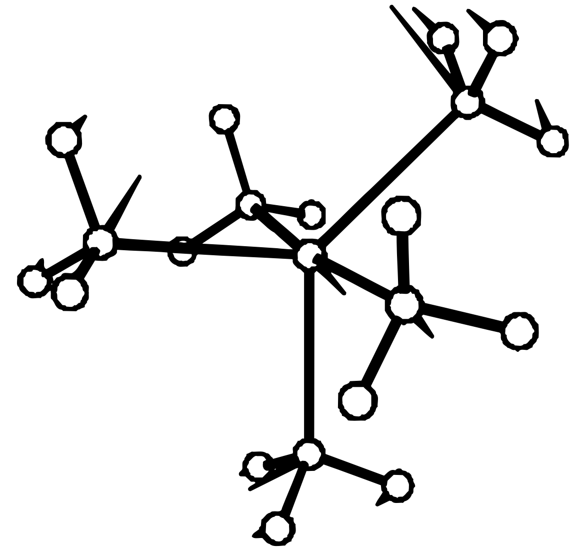


Figure 6. Perspective view and imaginary mode of the trigonal bipyramidal pentacoordinated transition state $[Cr(NH_3)_5^{3+}]^‡$.

Discussion

Effect of the Spectator Ligands (L_s) on the M···O Bond Lengths in the Transition States. For the first 6 water exchange reactions listed in Table 3, the associative interchange (I_a) pathway proceeding with retention of the configuration operates, and the structures of their transition states are analyzed in the following in more detail. The basicity of the spectator ligands L_s increases from the top to the bottom. When the 4 equatorial H_2O ligands in the transition state [*cis*-$Cr(OH_2)_5\cdots(OH_2)_2^{3+}]^‡$ are replaced by 4 NH_3 ligands, $d(Cr\cdots O)_{av}$ increases by 0.17 Å; the replacement of one equatorial H_2O by one NH_3 ligand leads to an elongation of $d(Cr\cdots O)_{av}$ by about 0.04 Å. When in the transition state $[Cr(NH_3)_4OH_2\cdots(OH_2)_2^{3+}]^‡$, the (spectator) aqua ligand (which is trans to the two exchanging H_2O molecules) is replaced by a NH_3 ligand, $d(Cr\cdots O)_{av}$ increases by 0.23 Å. This effect is 5−6 times larger than that of one cis ligand. Increasing the basicity of the ammonia ligand trans to the exchanging water ligands in [*cis*-$Cr(NH_3)_5\cdots(OH_2)_2^{3+}]^‡$ by its replacement with NH_2CH_3 produces a further increase of $d(Cr\cdots O)_{av}$ by 0.11 Å. If it is assumed that the influence of the cis and trans ligands on $d(Cr\cdots O)_{av}$ is as in the series $Cr(OH_2)_6^{3+}$ → *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ → $Cr(NH_3)_5OH_2^{3+}$ → *trans*-$Cr(NH_3)_4(NH_2CH_3)OH_2^{3+}$, one would estimate that the replacement of the equatorial NH_3 ligands of *trans*-$Cr(NH_3)_4(NH_2CH_3)OH_2^{3+}$ by 4 NH_2CH_3 groups would produce an elongation of $d(Cr\cdots O)_{av}$ by $0.11 \times 0.17/0.23 = 0.08$ Å. This means that, if in the transition state [*cis*-$Cr(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^‡$, the length of the Cr···O bonds would be determined merely by the basicity of the spectator ligands, a value of about 3.0 Å would be estimated, which is lower by more than 0.3 Å than the quantum chemically computed $d(Cr\cdots O)_{av}$ for the I_d pathway. The much longer Cr···O bonds in the transition state [*cis*-$Cr(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^‡$ arise from the steric repulsion caused by the bulky NH_2CH_3 ligands in equatorial position. It is furthermore striking that $d(Cr\cdots O)_{av}$ in this transition state is longer than $d(Rh\cdots O)_{av}$ in [*cis*-$Rh(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^‡$,

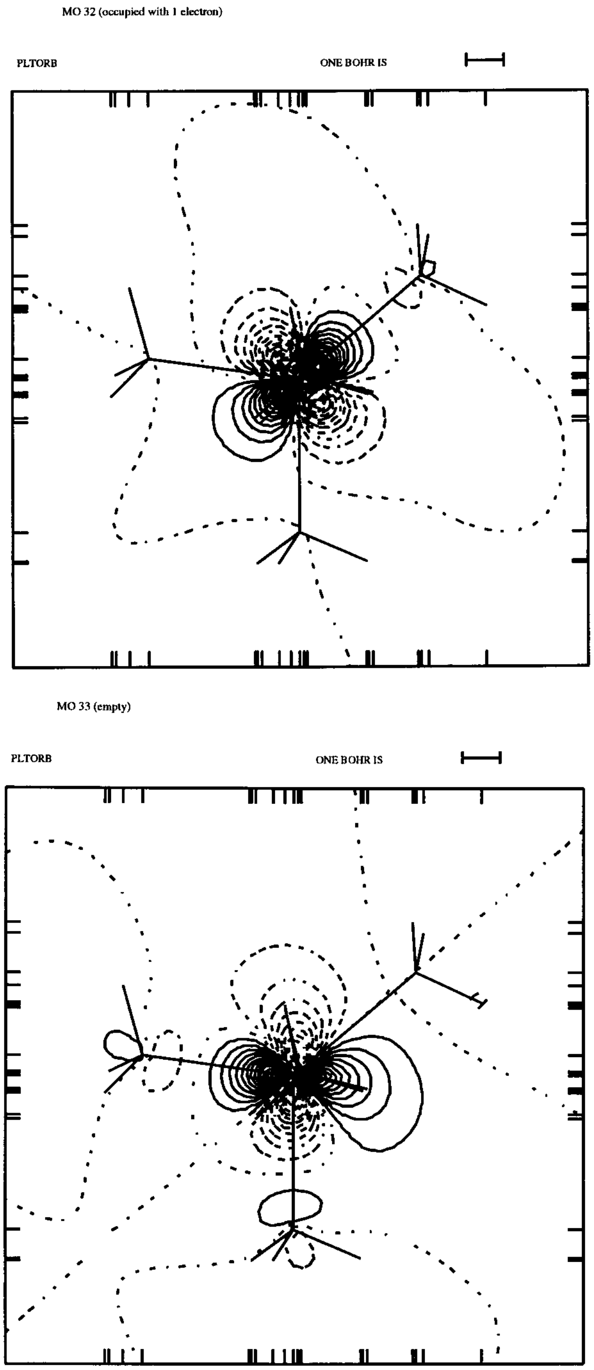


Figure 7. Contour plots depicting the 3d orbitals of $[Cr(NH_3)_5^{3+}]^{‡}$ in the trigonal plane: (a) singly occupied antibonding orbital, MO 32; (b) empty antibonding orbital, MO 33.

because in the latter, having a low-spin d^6 electron configuration, there is one additional antibonding d_{β} electron (Figure 3) than in the Cr^{III} species. In this case, the steric effects dominate the electronic ones. The latter can be rationalized in a straightforward manner,[4,10,11] but the steric effects are difficult to predict because in the transition state $[cis\text{-}Cr(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{‡}$ (Figure 1) all 5 CH_3 groups are located in the lower half of the pseudo-octahedron which is represented by the CrN_5 chromophore; obvious unfavorable steric interactions cannot be seen.

The above-presented discussion on the bond lengths in the transition state $[cis\text{-}Cr(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{‡}$ relates to the hypothesis, that reaction 5 proceeds via the I_d mechanism, but it should be remembered that the present model does not allow the distinction of the I_d form the D mechanism. All other exchange reactions (eqs 4, 6, 7, 8, and 9) proceed via the I_a pathway. The data in Table 3 shows that the increase in basicity of the spectator ligands causes an increase of $d(Cr\cdots O)_{av}$ by 0.5 − 0.6 Å. The same trend can be observed for the $\Delta\Sigma d(Cr-L)$ and $\Delta V^{‡}$ values. Therefore, $\Delta V_{int}^{‡}$ increases (becomes less negative) with increasing basicity of the spectator ligands. This relationship is also valid for the Ru^{III} complexes $Ru(OH_2)_6^{3+}$ and $Ru(NH_3)_5OH_2^{3+}$ (Table 3), and furthermore, for all other systems, in which the exchange or substitution reaction is not accompanied by spin changes.

For the interchange pathway with retention of the configuration, the replacement of the 5 NH_3 ligands in $Cr(NH_3)_5OH_2^{3+}$ by the 5 bulky NH_2CH_3 ones leads to a changeover in the exchange mechanism from I_a to I_d. It is interesting to note that the Cr···O bond length in the transition state $[Cr(NH_3)_5\cdots OH_2^{3+}]^{‡}$ for the hypothetical D mechanism of reaction 4 is nearly the same as that in $[Cr(NH_2CH_3)_5\cdots OH_2^{3+}]^{‡}$, and so are also the corresponding $\Delta\Sigma d(Cr-L)$ values, despite the bulky ligands (Table 2). Unlike the structures of the transition states for the interchange pathway, those for the D mechanism are quite insensitive to the bulkiness of the spectator ligands. The more bulky ligands just give rise to a lower activation energy for the D mechanism (by 17 kJ/mol) because of the relief of strain in the transition state (Table 1).

Stereochemistry and Comparison of Cr^{III} and Ru^{III}. All presently investigated exchange reactions on Cr^{III} and Ru^{III} complexes via the interchange pathway proceed with retention of the configuration. Bulky ligands may give rise to a dissociative (I_d or D) activation, and if the reaction proceeds via the D mechanism, the square pyramidal pentacoordinated intermediates, for example $Cr(NH_3)_5^{3+}$ and $Cr(NH_2CH_3)_5^{3+}$, are unlikely to rearrange according to eq 10 because their activation energies are considerably higher than those for water addition (Table 1).

For Ru^{III}, the situation with respect to the interchange mechanism and the rearrangement of the pentacoordinated intermediate via eq 10 is the same as for Cr^{III}. As already mentioned, for these two metal ions, the electronic structures of the (heptacoordinated) transition states differ by the number of electrons in the *nonbonding orbitals* only; the two nonbonding d_{α} levels[4,10,11] (Figure 3) are occupied by 2 and 4 electrons in the transition states of Cr^{III} and Ru^{III}, respectively. Disparate occupations of nonbonding molecular orbitals do not have pronounced effects on the structures. The third or fifth d electron of Cr^{III} or Ru^{III}, respectively, is located in the lower of the two (moderately) antibonding d_{β} levels. Thus, in both transition states, there is one electron in an antibonding orbital, and this is the reason that the structures of the transition states for the water exchange on the hexaaqua and aqua pentaammine complexes of Cr^{III} and Ru^{III} are so similar (Tables 2 and 3).

The water exchange reaction on $Ru(NH_3)_5OH_2^{3+}$ follows the I_a mechanism with retention of the configuration.[9] The situation for the rearrangement of a (putative) square pyramidal pentacoordinated intermediate of Ru^{III} is the same as that for Cr^{III} because the d_{π} orbital[15] (MO 31, Figure 5 (a)) in the plane, in which the motion of one NH_3 ligand will take place, is also singly occupied. In the transition state $[Ru(NH_3)_5^{3+}]^{‡}$, there would also be a single electron in an antibonding orbital as in Cr^{III} (MO 32, Figure 7 (a)). Transition states in which this orbital is occupied by two electrons can be imagined, but their energy will be much higher, and therefore, they are irrelevant. The substitution chemistry of Ru^{III} is very similar to that of Cr^{III}

TABLE 3: Comparison of d(M···O)$_{av}$, ΔΣd(M−L), and Δ$V^{‡}$ for Water Exchange Reactions via the Interchange Pathway with Retention of the Configuration

reactant	eq	d(M···O)$_{av}$, Å	ΔΣd(M−L), Å	Δ$V^{‡}$,[a] cm^3/mol
$Cr(OH_2)_6^{3+}$	3	2.40	−0.98	−9.6
$Ru(OH_2)_6^{3+}$	4	2.43	−0.97	−8.3
trans-$Cr(NH_3)_4(OH_2)_2^{3+}$	5	2.57	−0.92	
$Cr(NH_3)_5OH_2^{3+}$	1	2.80	−0.57	−5.8
$Ru(NH_3)_5OH_2^{3+}$	b	2.69	−0.82	−4.0
trans-$Cr(NH_3)_4(NH_2CH_3)OH_2^{3+}$	6	2.91	−0.36	
$Cr(NH_2CH_3)_5OH_2^{3+}$	2	3.32	0.33	−3.8
$Rh(NH_2CH_3)_5OH_2^{3+}$	c	3.22	0.15	1.2

[a] References 5, 7, 12, 13, and 14. [b] Reference 9. [c] Reference 10.

because of the presence of at least one singly occupied d_π orbital, together with the two empty d_σ* levels,[15] in the reactants of both metals.

Rh^{III} complexes exhibit an additional electron compared with those of Ru^{III}. The rearrangement of a putative pentacoordinated intermediate of Rh^{III} via eq 10 would involve a *doubly occupied antibonding orbital* (MO 32, Figure 7 (a)) in the trigonal bipyramidal transition state, which therefore would have a considerably higher energy than that of Ru^{III} (or Cr^{III}). Because of the large crystal field splitting parameter in second-row transition metals, it is unlikely, that a triplet electronic state is more stable. Whether an interchange or the dissociative mechanism operates, the substitution reactions on Rh^{III} proceed with retention of the configuration.[10]

Comparison of Cr^{III} with Co^{III} and Rh^{III}. Amine complexes of Co^{III} and Rh^{III} are valence isoelectronic and both exhibit a d^6 low-spin electron configuration. In the reactants, for example $M(NH_3)_5OH_2^{3+}$ (M = Cr, Ru, Co, Rh) complexes, only nonbonding orbitals are populated (Figure 3), and this is the reason these complexes are inert toward substitution. It has been shown in the Results section, that the reactivity of Cr^{III} and Ru^{III} is similar because in the transition states for the water exchange one (moderately) antibonding d_β orbital (Figure 3) is populated by one electron. In complexes of Co^{III} and Rh^{III}, the two d_α levels are occupied with 4 electrons, and the lower d_β level is populated by a *pair* of electrons. This pair of electrons is responsible for the substantially longer average Rh···O bonds of 3.13 Å in the transition state for the water exchange on $Rh(NH_3)_5OH_2^{3+}$ [10] compared with the structurally similar transition states of Cr^{III} and Ru^{III}, in which the Cr···O and Ru···O[9] bonds are considerably shorter (by 0.33 and 0.44 Å, respectively).

The Co··· Cl and Co···O bonds in the transition state for the aquation (substitution by water) of $Co(NH_3)_5Cl^{2+}$ are longer by 0.42 and 0.41 Å than the respective Cr···Cl and Cr···O bonds in the structurally similar transition state for the analogous reaction of $Cr(NH_3)_5Cl^{2+}$.[16]

The important difference between the low-spin d^6 systems (Co^{III} and Rh^{III}) on one hand and the high-spin d^3 (Cr^{III}) and the low-spin d^5 (Ru^{III}) systems on the other hand is that in the d^6 systems there is an additional electron in one *antibonding* d_β orbital (Figure 3). This additional d_β elecrtron is responsible for the longer Rh···O or Co···O bonds in the transition states (for the interchange mechanism with retention of the configuration) in comparison with the analogous species of Cr^{III} or Ru^{III}.

Computational Details

All of the calculations have been performed on Cray T3D, HP 9000/C200, and HP 9000/735 computers using the GAMESS[17] programs.

The basis sets of Stevens, Basch, Krauss, and Jasien[18] were used for chromium, where the 1s, 2s, and 2p shells are represented by relativistic effective core potentials, the 3s, 3p, 4s, and 4p shells have double-ζ quality, and the 3d triple-ζ quality. For ruthenium, an analogous basis set[18] has been used. For C, N, O, and H, 6-31G(d) basis sets[19,20] (basis set A) were used (α_{3d} = 0.80, 1.00, and 1.20,[21] respectively). In basis set B, the polarization functions on the C atoms were omitted.

In all of the geometry optimizations, the surrounding solvent (second and further coordination spheres) was represented by a dielectric continuum using the self-consistent reaction field model (SCRF),[22−24] as reported in earlier work.[9−11,16,25] These computations were performed at the Hartree−Fock level with the exception of that of the trigonal bipyramidal pentacoordinated transition state $[Cr(NH_3)_5^{3+}]^{‡}$ in its doublet electronic state, which required complete active space self-consistent field (CAS−SCF) calculations because of appreciable static electron correlation. The total energy of the hydrated ions was computed using the polarizable continuum model[26−28] at the CAS−SCF level, and dynamic electron correlation was taken into account using the multiconfigurational self-consistent field second-order quasidegenerate perturbation method (MCQDPT2)[29,30] as described.[9−11] The active space was determined as follows: first, the Hartree−Fock orbitals were localized using the population method.[31] Then, a first CAS−SCF calculation with an active space involving all σ(Cr−L) orbitals, the three d_π(Cr), and the two d_σ*(Cr) orbitals[15] was performed without converging it (10−25 iterations). Subsequently, the three natural orbitals with the highest occupations (>1.99) were removed from the active space. This lead to active spaces with a maximum size of 7 electrons in 7 orbitals. In some cases, the CAS−SCF calculations with this active space did not converge because there were still natural orbitals with occupations >1.99 and <0.01. After the removal of such orbitals from the active space, convergence was reached. The aqua complexes of Ru^{III} required an active space of 5 electrons in the 5 4d orbitals. There is no static electron correlation in the aqua complexes of Cr^{III} as already seen for the aqua ions of V^{II}, Mn^{II}, and Fe^{II}.[11] In the final CAS−SCF calculations, the occupations of the natural orbitals were <1.99 and >0.01; natural orbitals with occupations >1.99 or <0.01 were considered to give rise to dynamic electron correlation, and this contribution is included in the subsequent MCQDPT2 step. All of the atomic coordinates are summarized in Tables S1−S24 (Supporting Information).

Summary

(i) In the absence of bulky ligands, the water exchange reaction on aqua amine complexes of Cr^{III} proceeds via the I$_a$ mechanism with retention of the configuration. (ii) The length of the two Cr···O bonds in the transition state depends on the basicity of the equatorial and axial ligands, whereas the effect of the trans ligand is larger than that of those in cis position. (iii) The longer d(Cr···O)$_{av}$ or the larger (less negative) ΔΣd(M−L), the larger (less negative) is $\Delta V_{int}^{‡}$. (iv) Bulky ligands such as NH_2CH_3 give rise to a changeover in mechanism; water exchange on $Cr(NH_2CH_3)_5OH_2^{3+}$ proceeds via a dissociative activation. In this case, the steric repulsion dominates over the electronic effects which would favor short Cr···O bonds (and therefore the I_a mechanism). (v) The rearrangement of putative pentacoordinated intermediates, $Cr(NH_3)_5^{3+}$ and $Cr(NH_2CH_3)_5^{3+}$ for example, via trigonal bipyramidal transition states, requires activation energies which are substantially larger than those for water addition. Therefore, also substitution reactions on Cr^{III} which would follow the D mechanism, would proceed with retention of the configuration. (vi) The rearrangement of pentacoordinated intermediates of Ru^{III} would have a similar activation energy, and that of Rh^{III} an even larger one.

Acknowledgment. The “Service Informatique Central” is acknowledged for computer time on the Cray T3D.

Supporting Information Available: A listing of the atomic coordinates of all reactants/products, transition states, pentacoordinated intermediates, and pentacoordinated transition states (Tables S1−S24). This information is available free of charge via the Internet at http://pubs.acs.org.

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(2) $\Delta E^{\ddagger}$ corresponds to the activation enthalpy at 0 K without the contributions of the zero point energies.

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