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Mechanism of the S → N Isomerization and Aquation of the Thiocyanato Pentaammine Cobalt(III) Ion

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All of the stationary points on the potential energy surface of the S → N isomerization and aquation of the $Co(NH_3)_5SCN^{2+}$ ion have been investigated with ab initio quantum chemical methods. Also the corresponding anations of the $Co(NH_3)_5OH_2^{3+}$ ion by the N and S ends of SCN^- and the substitution of thiocyanate via the D mechanism have been studied. All calculations have been performed by taking into account hydration. The most favorable reaction of $Co(NH_3)_5SCN^{2+}$ is the isomerization. It is concerted, follows the I or I_d mechanism, depending on the applied criteria, and proceeds via a T-shaped transition state. The aquations of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ and the corresponding inverse reactions, the anations, all proceed via the I_d mechanism. The activation energies, calculated for the isomerization and aquation, agree with experiment, and so does the difference of the activation energies for the anations by the two donors of SCN^-. This energy difference reflects the disparate nucleophilicities of the N and S ends of SCN^- and shows that bond making in the transition state is significant for the I_d mechanism. Isomerization and aquation are two parallel reactions which proceed via two disparate transition states. The computed activation energy for the SCN^- substitution via the D mechanism is the highest, and therefore, this pathway is unlikely to operate for the isomerization and aquation of $Co(NH_3)_5SCN^{2+}$. The S → N isomerization and the SCN^- substitution via the D mechanism were furthermore computed for the free ions in the gas phase: the isomerization would require a higher activation energy and follow the I_a mechanism. The activation energy for the SCN^- substitution via the D mechanism would be very high, because of the large electrostatic work which is required for the removal of an anion from a (formally) 3+ charged cation.

Introduction

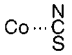
The S → N isomerization of the thiocyanato pentaammine complex of cobalt(III) (reaction 1) has been investigated extensively over more than 20 years[1] with the aim of determining the substitution mechanism involved in the spontaneous ligand substitution reactions of pentaamine complexes of cobalt(III).[2]

$$Co(NH_3)_5SCN^{2+} \rightarrow Co(NH_3)_5NCS^{2+} \qquad (1)$$

For the spontaneous aquation of the neutral X group in $Co(NH_3)_5X^{3+}$ complexes, the dissociative nature of the substitution process has been established.[3] The relatively small but positive volumes of activation (0.3−3.8 $cm^3\ mol^{-1}$) support a dissociative interchange (I_d) mechanism.[3] A dissociative (D) mechanism, proceeding via a pentacoordinated intermediate, has also been invoked, but neither the existence nor the nonexistence of such a pentacoordinated intermediate has been substantiated so far.

It is noteworthy that, in the thiocyanato pentaamine complexes of cobalt(III), the nucleophile, namely, the N end of the thiocyanato ligand, is already present in the reactant. Therefore, the isomerization reaction (eq 1) might be considered as an intramolecular substitution process, where the N end of thiocyanate acts as the nucleophile and the S end as the leaving group.

For the isomerization of the thiocyanato pentaammine cobalt(III) ion, $Co(NH_3)_5SCN^{2+}$, in water ($I = 0.1$ M and 50 °C) the activation parameters $\Delta H^{\ddagger} = 102.8 \pm 0.8$ kJ mol^{-1}, $\Delta S^{\ddagger} = -14 \pm 3$ J K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = -5.3 \pm 0.8$ cm^3 mol^{-1} have been determined by Palmer et al.[4] They pointed out that the negative volume of activation argues against a dissociative mechanism and proposed an associative activation for the S → N isomerization. They suggested that this reaction proceeds via the T-shaped



transition state that had already been postulated in the very first investigation[5] of this reaction. The aquation (reaction 2), however, that occurs also to a small extent (≈10%) as a side reaction,[6] is an ordinary substitution process.

$$Co(NH_3)_5SCN^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + SCN^- \qquad (2)$$

Since the major product is $Co(NH_3)_5NCS^{2+}$,[6] this experiment argues against the release of SCN^- into the second coordination sphere during the isomerization. In order to obtain a further insight into the S → N isomerization and the aquation of the thiocyanato pentaammine cobalt(III) ion, reactions 1 and 2 were investigated using quantum chemical methods.

The anation of $Co(NH_3)_5OH_2^{3+}$ by the N and S ends of SCN^-, reaction 3, is of interest, because the structures and

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energies of the corresponding two transition states show the role of the nucleophilicity of the N and S ends of thiocyanate.

$$Co(NH_3)_5OH_2^{3+} + SCN^- \rightarrow Co(NH_3)_5SCN^{2+} + H_2O \quad (3a)$$

$$Co(NH_3)_5OH_2^{3+} + SCN^- \rightarrow Co(NH_3)_5NCS^{2+} + H_2O \quad (3b)$$

Of course, the transition state of reaction 3a is the same as that of 2, since 3a is just the inverse reaction 2.

In previous work, the mechanism of the water exchange of metal hexaaqua ions was investigated with ab initio methods based on a model[7] involving $M(OH_2)_6^{n+}$ or $M(OH_2)_7^{n+}$ species in the gas phase, by computations of the structures of the transition states and intermediates.[7−10] These calculations allowed the determination of the exchange mechanism, because each type of exchange mechanism (A, I_a, and D) proceeds via a characteristic transition state. It should be noted that, for the water exchange on hexaaqua ions,[7−10] no transition state for the I_d mechanism has been found. Such a transition state has, however, been obtained for the aquation of $Co(NH_3)_5Cl^{2+}$.[11]

The activation energies and structural changes involved in reactions 1−3 have been investigated using quantum chemical techniques. The results offer a detailed insight into the reaction mechanisms, in particular the intimate nature of the I_d mechanism. The effect of hydration is discussed on the basis of the isomerization and the substitutions on $Co(NH_3)_5SCN^{2+}$ via the D mechanism.

Results

Overview. The S → N isomerization (reaction 1) and the substitution of SCN^- via the D mechanism can be described with the components $Co(NH_3)_5^{3+}$ and SCN^-, which are called system 1. The aquation and anation reactions (2 and 3) involve the above-mentioned fragments and one water molecule, and the set of the these three components, $Co(NH_3)_5^{3+}$, SCN^-, and H_2O, is called system 2. For comparison with the aquations or anations, the isomerization has also been computed on the basis of system 2.

Hydration was included in the calculations of the geometry and energy of all species, since all reactions involve the SCN^- anion. For the isomerization and the substitution of SCN^- via the D mechanism, the structures and energies were also computed for the free ions in the gas phase on the basis of system 1. This data set shows the effect of hydration and shows that the present computational approach is adequate.

Since there is static electron correlation in these thiocyanato complexes (see Calculations on System 1. S → N Isomerization of $Co(NH_3)_5SCN^{2+}$), the geometry of the key species of the isomerization, the transition state $[Co(NH_3)_5\cdots CNS^{2+}]^‡$ which has C_s symmetry for system 1, was also optimized at the CAS-SCF level. Because the geometries obtained at the Hartree−Fock and CAS-SCF levels are marginally different, the computationally much less demanding Hartree−Fock method is adequate. It was applied to the calculation of all stationary points on the potential energy surfaces for the isomerization and substitution reactions.

Computational Methods and Approximations. For both systems, all calculations have been performed for the hydrated ions (at the Hartree−Fock level). The geometries were optimized using the self-consistent reaction field model (SCRF),[12−14] because this method is computationally efficient for this task, but it is not suitable for the evaluation of the energy, since the latter depends strongly on the cavity radius. The polarizable continuum model (PCM),[15−17] however, which does not suffer from this shortcoming, was used for the computations of the energy. The atomic coordinates of all hydrated ions are given in Tables S1−S5 (Supporting Information).

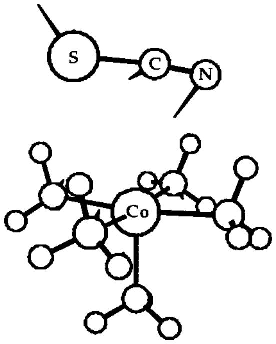

Figure 1. Structure and imaginary mode of the transition state $[Co(NH_3)_5\cdots CNS^{2+}]^‡$ (S → N isomerization, system 1).

As already mentioned, for the determination of the effect of hydration, the isomerization and the SCN^- substitution via the D mechanism have also been computed for the free ions in the gas phase on the basis of system 1.

Electron correlation has been neglected, because of the agreement of the calculated activation energies with experiment. It should be noted that, in a study[18] of the water exchange on $Ru(NH_3)_5OH_2^{3+}$, it has been shown that the computed activation energy depends critically on the effects of hydration, but not so on electron correlation.

The zero point vibrational energies (ZPVE) were neglected, because in the present models for the treatment of hydration, the *specific* solute−solvent interactions are not considered. The second coordination sphere and the bulk solvent are treated as a polarizable continuum. Since the partial charges on the SCN^- anion (and the $Co(NH_3)_5^{3+}$ fragment as well) change considerably during all activation processes, these specific interactions are expected to change, too. In the computation of the vibrational frequencies at the SCRF level, no specific solute−solvent interactions are taken into account. Since the changes of the ZPVE (at the SCRF level) for reactions 1−3 are smaller than 4 kJ/mol, their inclusion would not alter the activation energies significantly. For the interested reader, the ZPVEs are given in Tables S1−S5 (Supporting Information).

Calculations on System 1. S → N Isomerization of $Co(NH_3)_5SCN^{2+}$. This reaction system involves the $Co(NH_3)_5^{3+}$ and SCN^- components. The structures of the (hydrated) reactant $Co(NH_3)_5SCN^{2+}$ and product $Co(NH_3)_5NCS^{2+}$ are the same as those obtained for the isomerization on the basis of system 2, but of course without any water molecule in the second coordination sphere. The transition state $[Co(NH_3)_5\cdots CNS^{2+}]^‡$ is depicted in Figure 1. Its structure was computed in the following way: starting from the reactant (with C_1 symmetry), whose geometry was optimized first, the Co−S bond was

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Table 1. Calculated Total and Relative Energies, Experimental Activation Energies, and Change of the Sum of the Co−L Bond Lengths for the Free and the Hydrated Ions of System 1

	E, hartrees	$\Delta E^\ddagger$ or ΔE, kJ/mol	$\Delta G_{298}{}^\ddagger$, kJ/mol	$\Delta\Sigma d$(Co−L), Å
(i) Hydrated Ions[a]				
$Co(NH_3)_5SCN^{2+}$	−527.292049	0.0		0.0
$[Co(NH_3)_5\cdots CNS^{2+}]^\ddagger$	−527.250691[b]	108.6	106.9[c]	0.06
$Co(NH_3)_5NCS^{2+}$	−527.309262	−45.2		0.05
$[Co(NH_3)_5\cdots SCN^{2+}]^\ddagger$	−527.238918[d]	139.5		2.98
$Co(NH_3)_5\cdot SCN^{2+}$	−527.242612	129.8		2.55
(ii) Free Ions in the Gas Phase[e]				
$Co(NH_3)_5SCN^{2+}$	−526.962320	0.0		0.0
$[Co(NH_3)_5\cdots CNS^{2+}]^\ddagger$	−526.907806[f]	143.1	106.9[c]	−0.40
$Co(NH_3)_5NCS^{2+}$	−526.981041	−49.2		0.06
$[Co(NH_3)_5\cdots SCN^{2+}]^\ddagger$	−526.859811[g]	269.1		2.33
$Co(NH_3)_5\cdot SCN^{2+}$	−526.877994	221.4		2.07

[a] Geometry: SCRF model. Energy: PCM at the Hartree−Fock level. [b] Imaginary frequency: 151i cm^{-1}. [c] See Discussion. [d] Imaginary frequency: 64i cm^{-1}. [e] Geometry and energy calculated for the free ions in the gas phase. [f] Imaginary frequency: 208i cm^{-1}. [g] Imaginary frequency: 89i cm^{-1}.

elongated incrementally and held constant while all the other internal coordinates were optimized. This process mimicked a dissociative activation where the SCN^- ligand rearranged to form a T-shaped species, the computed vibrational spectrum of which exhibited an imaginary frequency. The elongation of the Co−S bond was concerted with the formation of the respective Co···N bond. The structure of this transition state was refined by following its imaginary mode (no constraint was applied). This species exhibits C_s symmetry, and the imaginary mode represents the reaction coordinate for the S → N isomerization (Figure 1). It should be noted that the SCN^- ion remains linear. The product with C_1 symmetry was obtained by the computation of the intrinsic reaction coordinate.

The geometries and energies of all three species involved in reaction 1 were computed for the free and the hydrated ions. Calculated total and relative energies, experimental activation energies, and the change of the sum of the Co−L bond lengths, $\Delta\Sigma d$(Co−L), for system 1 are reported in Table 1. The calculated activation energy ($\Delta E^\ddagger$) agrees with experiment for the hydrated ions, but not for the free ones, for which it is too high by 36 kJ/mol. In aqueous solution, the S → N isomerization is exergonic, and in agreement with this observation, the calculations predict that the N-bonded isomer is more stable than the S-bonded one (Table 1). Also in the gas phase or in solvents with low dielectric constants, $Co(NH_3)_5NCS^{2+}$ is expected to be the more stable isomer.

Selected bond lengths and angles of the three species involved in the isomerization, together with the corresponding data from crystal structures,[19] are reported in Table 2. The geometries optimized for the free ions in the gas phase deviate considerably from experiment, in particular the Co−N−C angle of the product $Co(NH_3)_5NCS^{2+}$, which is too small by at least 18°. More importantly, in the transition state, the SCN^- ligand is nearer to the cobalt(III) center by about 0.25 Å or more as shown by the Hartree−Fock (Table 2) and CAS-SCF calculations (see below and Table 3). The weak Co···CNS bond in the transition state is sensitive to hydration. The disparate Co···CNS distances of the free and the hydrated ion show that in general the structure of the transition states, in which there are always weak bonds, depends on the nature of the solvent, especially when cations and anions are involved in the reaction. It is interesting to note that in a solvent with a low dielectric constant, whereby the in vacuo calculations represent the limiting case where $\epsilon = 1$, the S → N isomerization is predicted to proceed via the I_a mechanism, because of the significantly negative $\Delta\Sigma d$(Co−L) value of −0.40 Å (Table 1 (ii)).

The Co−N(H_3) bonds of the reactant and product are approximately 0.08 Å longer than in the crystal structures[19] (Table 2). Neither the inclusion of hydration nor the treatment of static electron correlation with CAS-SCF calculations (next paragraph and Table 3) reduces this error. It arises mainly from the neglect of hydrogen bonding with water from the second coordination sphere and also from the neglect of dynamic electron correlation. Since this systematic error occurs in all species, it cancels out in the difference of the Co−N(H_3) bond length changes $\Delta\Sigma d$(Co−N(H_3)) (Table 2). Also hydrogen bonding of water with the SCN^- ligand is not taken into account by the SCRF and PCM models. Despite all of these unavoidable approximations, the present calculations yielded an activation energy for the isomerization and the other reactions (see next section), too, that agrees with experiment (Table 1). This is probably because of the inertness of the pentaamine complexes of cobalt(III).[20] The major contribution to the activation energy of such substitution reactions arises form the weakening or breaking of *strong* Co^{III}−L bonds. Changes in the hydration shell are considered at least partly with the SCRF and PCM models. Neglected are the *changes* in hydrogen bonding with water in the second coordination sphere, which are certainly small compared with all of the other contributions, in particular because hydrogen bonding of water with ammonia ligands is much weaker than with aqua ligands.

Since the transition state plays a key role in the rationalization of this reaction, computations treating electron correlation were also performed for the free and the hydrated cation. The effect of static electron correlation was analyzed by performing single reference singles-doubles CI (SR-SDCI) calculations using the iterative natural orbital method (INO).[21] These showed that there is considerable static electron correlation, and that the major contributions are due to the SCN^- ligand. Therefore, the geometry of the transition state has been optimized at the complete active space SCF (CAS-SCF) level with various active spaces, the largest one having 12 electrons in 12 orbitals, giving rise to 113616 configuration state functions. The large CAS-SCF calculation includes some dynamic correlation, and this is the reason why the Co···CNS distance is slightly shorter (by about 0.04 Å) than in the small calculation with only 12 configuration state functions (Table 3). For the hydrated and the free ions, the CAS-SCF geometries do not differ substantially from those obtained at the Hartree−Fock level and, more significantly, the nature of this species did not change; it remained a transition state exhibiting the imaginary mode shown in Figure 1. This shows that the Hartree−Fock level is adequate for the calculation of the geometry of the presently investigated species. Another important result is that the CAS-SCF calculations did not improve the too long Co−N(H_3) bonds.

SCN^- Substitution via the D Mechanism. The transition state $[Co(NH_3)_5\cdots SCN^{2+}]^\ddagger$ (Figure 2) for this pathway has C_s symmetry and was obtained by the elongation of the Co−S bond with a simultaneous rotation of the SCN^- ligand such that the N donor of thiocyanate was removed from the cobalt(III) center. Without rotation, the transition state for the isomerization (Figure

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(20) The pentaamine complexes of cobalt(III) are inert, since in their low-spin d^6 electron configuration which gives rise to a singlet electronic state, merely nonbonding orbitals are occupied.

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Table 2. Selected Calculated (Hartree−Fock Level) and Experimental[19] Bond Lengths and Angles of the Reactant $Co(NH_3)_5SCN^{2+}$, Transition State $[Co(NH_3)_5\cdots CNS^{2+}]^{\ddagger}$, and Product $Co(NH_3)_5NCS^{2+}$ of the Isomerization (System 1)

internal coordinate[a]	$Co(NH_3)_5SCN^{2+}$ calcd[b]	$Co(NH_3)_5SCN^{2+}$ exptl	$[Co(NH_3)_5\cdots CNS^{2+}]^{\ddagger}$ calcd[b]	$Co(NH_3)_5NCS^{2+}$ calcd[b]	$Co(NH_3)_5NCS^{2+}$ exptl
d(Co−N(H$_3$))[c]	2.04 (2.05)	1.965−1.984	2.00 (2.00)	2.04 (2.04)	1.94−1.948
d(Co−S)	2.38 (2.34)	2.299−2.308	3.51 (3.27)	4.67 (4.50)	4.68
d(Co−C)	3.19 (3.08)	3.159−3.172	3.12 (2.86)	3.07 (2.97)	3.06
d(Co−N(CS))	4.00 (3.83)	4.083−4.090	3.22 (2.97)	1.91 (1.88)	1.92
α(Co−S−C)	101.4 (98.3)	105.6−107	62.6 (60.7))		
α(Co−N−C)			74.4 (73.2)	177.5 (151.9)	170.1
α(S−C−N)	176.2 (172.3)	178.2−178.6	173.7 (172.3)	179.9 (179.8)	178.8
d(S−C)	1.70 (1.70)	1.652−1.661	1.68 (1.67)	1.60 (1.58)	1.63
d(C−N)	1.14 (1.14)	1.143−1.152	1.15 (1.15)	1.16 (1.18)	1.16
$\sum d$(Co−L)	19.78 (19.51)	19.42	19.84 (19.11)	19.83 (19.57)	19.56
$\sum d$(Co−CNS)	9.57 (9.26)	9.56	9.85 (9.10)	9.65 (9.36)	9.66
$\sum d$(Co−N(H$_3$))	10.21 (10.25)	9.87	9.99 (10.02)	10.18 (10.21)	10.20

[a] Bond lengths (d) in angstroms; bond angles (α) in degrees. [b] In parentheses: geometry of the free ion (without hydration). [c] Average.

Table 3. Selected Bond Lengths and Bond Angles of the Transition State $[Co(NH_3)_5\cdots CNS^{2+}]^{\ddagger}$ Calculated at the CAS-SCF Level (System 1)[a]

internal coordinate[b]	active space (no. of electrons, no. of orbitals, no. of configuration state functions) 4, 4, 12[c]	6, 6, 95	8, 8, 924	12, 12, 113616
d(Co−N(H$_3$))[d]	2.00 (2.00)	2.00	2.00	2.00 (2.01)
d(Co−S)	3.54 (3.30)	3.56	3.57	3.51 (3.24)
d(Co−C)	3.12 (2.86)	3.14	3.14	3.06 (2.73)
d(Co−N(CS))	3.21 (2.97)	3.22	3.23	3.18 (2.87)
α(Co−S−C)	61.9 (60.0)	61.9	61.7	60.7 (57.1)
α(Co−N−C)	74.8 (73.1)	75.9	75.1	73.4 (70.8)
α(S−C−N)	173.5 (173.2)	172.3	173.1	175.5 (176.6)
d(S−C)	1.69 (1.68)	1.72	1.72	1.68 (1.68)
d(C−N)	1.17 (1.17)	1.17	1.18	1.19 (1.19)

[a] In parentheses: values for the free ion in the gas phase. [b] Bond lengths (d) in angstroms; bond angles (α) in degrees. [c] Imaginary vibrational frequency for the hydrated ion: 151i cm^{-1}. [d] Average.

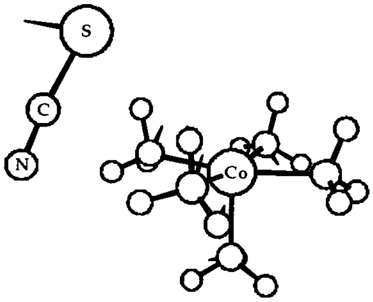

Figure 2. Structure and imaginary mode of the transition state $[Co(NH_3)_5\cdots SCN^{2+}]^{\ddagger}$ (SCN^- substitution via the D mechanism, system 1).

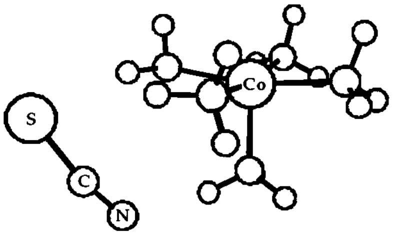

Figure 3. Structure of the pentacoordinated intermediate $Co(NH_3)_5\cdot SCN^{2+}$ (SCN^- substitution via the D mechanism, system 1).

1) is obtained. The structure of the corresponding pentacoordinated intermediate $Co(NH_3)_5\cdot SCN^{2+}$ (Figure 3), which has also C_s symmetry, was obtained by the computation of the intrinsic reaction coordinate. In this species, the sulfur donor atom is removed entirely from its original coordination site. This pathway was investigated for the demonstration that it is competitive neither with the S → N isomerization (Table 1) nor with the aquation (see next section). For the free ions in the gas phase, and also in solutions having low dielectric constants, the activation energy ($\Delta E^{\ddagger}$) for this pathway is very high, and so is the relative energy (ΔE) of the pentacoordinated intermediate (Table 1). These high energies ($\Delta E^{\ddagger}$ and ΔE) reflect the Coulomb work which is required for the separation of an anion from a cation with a (formal) 3+ charge. In aqueous solution, and also in solvents with high dielectric constants, these energies are considerably lower, but both, the activation energy for the elimination of SCN^- and the relative energy of the pentacoordinated intermediate, are higher than the activation energy for the isomerization (reaction 1) and the aquation (reaction 2) via the I_d mechanism (see next section).

Calculations on System 2. The key species in reactions 1−3 are the transition states. Reactions 2 and 3 involve the $Co(NH_3)_5^{3+}$ fragment, the SCN^- anion, and at least one H_2O molecule. The transition state for the S → N isomerization and those for the aquations of both $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ (or the anations of $Co(NH_3)_5OH_2^{3+}$ by the N and S ends of SCN^-) were computed starting from a square pyramidal $Co(NH_3)_5^{3+}$ fragment with the SCN^- and H_2O groups in proximity of the free coordination site. The geometries of the three transition states have been optimized by following the appropriate imaginary mode.

These calculations have been performed for the hydrated ions only. The corresponding calculated and experimental energies, together with the $\Delta\sum d$(Co−L)) values are reported in Table 4, and selected bond lengths and angles for reactions 1 and 2 are given in Tables 5 and 6, respectively.

S → N Isomerization. The structure of the transition state $[Co(NH_3)_5\cdots CNS\cdot OH_2^{2+}]^{\ddagger}$ (Figure 5) was calculated as described above. The reactant $Co(NH_3)_5SCN\cdot OH_2^{2+}$ (Figure 4), the water adduct of $Co(NH_3)_5SCN^{2+}$, and the product $Co(NH_3)_5OH_2\cdot SCN^{2+}$ (Figure 6), also as the water adduct, were obtained by computations of the corresponding intrinsic reaction coordinates. The transition state, exhibiting a linear SCN^- group (Table 5), is the same T-shaped species as in system 1. The water molecule in the second coordination sphere does not participate in this reaction. It is hydrogen bonded to two adjacent ammonia ligands, and there is no local minimum for this water located closer to the SCN^- ligand. The imaginary mode (Figure 5) is the reaction coordinate for the S → N isomerization that describes the concerted elongation of the Co···S and the formation of the Co···N(CS) bonds. As for system 1, no

Table 4. Calculated Total and Relative Energies, Experimental Activation Energies, and Change of the Sum of the Co−L Bond Lengths for the Hydrated Ions of System 2

	E, hartrees	$\Delta E^\ddagger$ or ΔE, kJ/mol	$\Delta G_{298}{}^\ddagger$, kJ/mol	$\Delta\Sigma d$(Co−L), Å
	(i) S → N Isomerization of $Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$			
$Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$	−603.322445[a]	0.0		0.0
$[Co(NH_3)_5{\cdots}CNS{\cdot}OH_2{}^{2+}]^\ddagger$	−603.282293[b]	105.4	106.9[c]	−0.02 (−0.07[d])
$Co(NH_3)_5NCS{\cdot}OH_2{}^{2+}$	−603.336740	−37.5		0.06
	(ii) Aquation of $Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$			
$Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$	−603.322445[a]	0.0		0.0
$[Co(NH_3)_5{\cdots}(SCN)(OH_2)^{2+}]^\ddagger$	−603.276890[e]	119.6	112.7[c]	1.84
$Co(NH_3)_5OH_2{\cdot}SCN^{2+}$	−603.317415	13.2		1.07
	(iii) Aquation of $Co(NH_3)_5NCS{\cdot}OH_2{}^{2+}$ [f]			
$[Co(NH_3)_5{\cdots}(NCS)(OH_2)^{2+}]^\ddagger$	−603.278515[g]			

[a] Within the error limits, these two reactants are mirror images of each other. The energy is the average (see text). [b] Imaginary frequency: 152i cm^{-1}. [c] See Discussion. [d] This value includes *d*(Co···O(H$_2$)). [e] Imaginary frequency: 108i cm^{-1}. [f] Inverse reaction 3b. [g] Imaginary frequency: 140i cm^{-1}.

Table 5. Selected Calculated Bond Lengths and Angles of the Reactant, Transition State, and Product of the Isomerization (System 2)

internal coordinate[a]	$Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$	$[Co(NH_3)_5{\cdots}CNS{\cdot}OH_2{}^{2+}]^\ddagger$	$Co(NH_3)_5NCS{\cdot}OH_2{}^{2+}$
d(Co−N(H$_3$))[b]	2.04	1.99	2.03
d(Co−S)	2.38	3.48	4.68
d(Co−C)	3.19	3.09	3.07
d(Co−N(CS))	4.00	3.20	1.91
α(Co−S−C)	101.2	62.7	
α(Co−N−C)		73.8	174.9
α(S−C−N)	176.2	173.8	179.9
d(S−C)	1.70	1.68	1.61
d(C−N)	1.14	1.15	1.16
d(Co···O)	4.03	3.98	4.03
Σ*d*(Co−L)	23.79 (19.76[c])	23.72 (19.74[c])	23.85 (19.82[c])
Σ*d*(Co−CNS)	9.57	9.77	9.66
Σ*d*(Co−N(H$_3$))	10.19	9.97	10.16

[a] Bond lengths (d) in angstroms; bond angles (α) in degrees. [b] Average. [c] *d*(Co···O) not included.

Table 6. Selected Calculated Bond Lengths and Angles of Species Involved in Aquations or Anations (System 2)

internal coordinate[a]	$Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$	$[Co(NH_3)_5{\cdots}(SCN)(OH_2)^{2+}]^\ddagger$	$Co(NH_3)_5OH_2{\cdot}SCN^{2+}$	$[Co(NH_3)_5{\cdots}(NCS)(OH_2)^{2+}]^\ddagger$
d(Co−N(H$_3$))[b]	2.04	1.99	2.03	1.99
d(Co−S)	2.38	3.94	4.54	5.84
d(Co−C)	3.18	4.09	4.12	4.22
d(Co−N(CS))	4.00	4.49	4.08	3.05
α(Co−S−C)	101.1	83.1		
α(Co−N−C)				179.9
α(S−C−N)	176.3	175.3	173.3	179.5
d(S−C)	1.70	1.69	1.68	1.62
d(C−N)	1.14	1.14	1.15	1.17
d(Co−O)	4.03	3.13	1.98	2.84
Σ*d*(Co−L)	23.78	25.62	24.85	25.92
Σ*d*(Co−CNS)	9.56	12.52	12.74	13.11
Σ*d*(Co−N(H$_3$))	10.19	9.97	10.13	9.97

[a] Bond lengths (*d*) in angstroms; bond angles (α) in degrees. [b] Average.

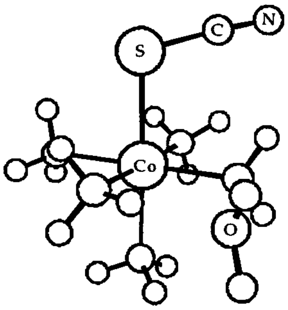

Figure 4. Structure of the reactant $Co(NH_3)_5SCN{\cdot}OH_2{}^{2+}$ (S → N isomerization, system 2).

intermediate was found on this reaction path and, therefore, the isomerization follows an interchange mechanism.

The transition state, $[Co(NH_3)_5{\cdots}CNS^{2+}]^\ddagger$, calculated on the basis of system 1 (Figure 1 and Table 2), has Co−N(H$_3$) and Co···CNS bond lengths that are similar to those of $[Co(NH_3)_5{\cdots}CNS{\cdot}OH_2{}^{2+}]^\ddagger$ (Figure 5 and Table 5). Also the corresponding ΔΣ*d*(Co−N(H$_3$)) and ΔΣ*d*(Co−L) parameters are the same within error limits; therefore, on the basis of this data, the same reaction mechanism, I or I$_d$ depending on the preferred criterion, is attributed to the S → N isomerization (see Discussion). The calculated activation energy agrees with experiment (Table 4), and it is insensitive to the added water molecule.

Aquation of $Co(NH_3)_5SCN^{2+}$. The reactant (Figure 7) and product (Figure 9) of reaction 2 were obtained by computations of the intrinsic reaction coordinates. The imaginary mode (Figure 8) of the transition state $[Co(NH_3)_5{\cdots}(SCN)(OH_2)^{2+}]^\ddagger$ describes the elongation of the Co···S bond which is concerted with the formation of the Co···O bond.[22] Also this reaction (eq 2) follows

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(22) The Mulliken charge of the SCN$^-$ ligand in this transition state is −0.82. This establishes that the SCN$^-$ *anion* is substituted by water.

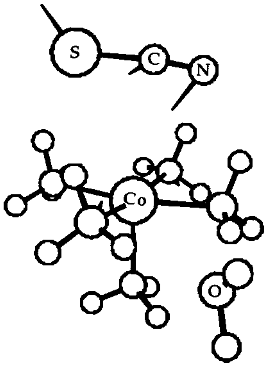

Figure 5. Structure and imaginary mode of the transition state $[Co(NH_3)_5\cdots CNS\cdot OH_2^{2+}]^{\ddagger}$ (S → N isomerization, system 2).

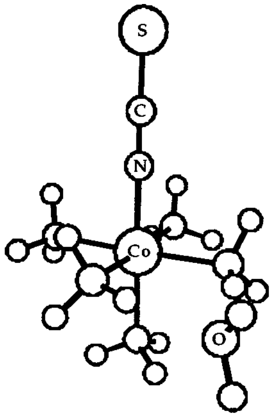

Figure 6. Structure of the product $Co(NH_3)_5NCS\cdot OH_2^{2+}$ (S → N isomerization, system 2).

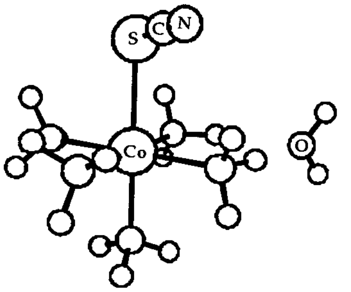

Figure 7. Structure of the reactant $Co(NH_3)_5SCN\cdot OH_2^{2+}$ (aquation of $Co(NH_3)_5SCN^{2+}$, system 2).

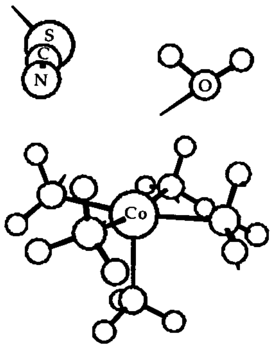

Figure 8. Structure and imaginary mode of the transition state $[Co(NH_3)_5\cdots(SCN)(OH_2)^{2+}]^{\ddagger}$ (aquation of $Co(NH_3)_5SCN^{2+}$, system 2).

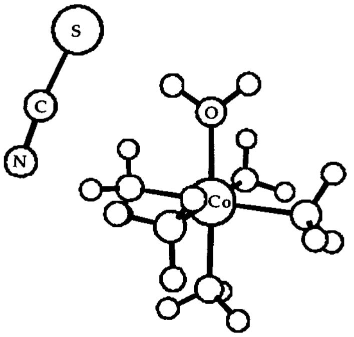

Figure 9. Structure of the product $Co(NH_3)_5OH_2\cdot SCN^{2+}$ (aquation of $Co(NH_3)_5SCN^{2+}$, system 2).

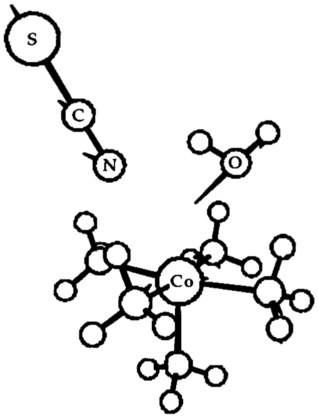

Figure 10. Structure and imaginary mode of the transition state $[Co(NH_3)_5\cdots(NCS)(OH_2)^{2+}]^{\ddagger}$ (aquation of $Co(NH_3)_5NCS^{2+}$, system 2).

an interchange mechanism, since no intermediate was found on the reaction paths. Selected bond lengths and angles are summarized in Table 6. The reactant, $Co(NH_3)_5SCN\cdot OH_2^{2+}$, is the mirror image of that of reaction 1 (system 2); otherwise they are identical. The small differences in the structures (Tables 5 and 6) lie within the error limits of the calculations. This is the reason why in Table 4 the energies of the reactants of the isomerization and aquation were averaged.

The calculated activation energy for this pathway agrees also with experiment (Table 4), and it is higher than that for the isomerization, but lower than that for the D mechanism (Table 1). Therefore, the aquation most likely proceeds via the I_d and not via the D mechanism. In agreement with experiment, the calculations predict that the isomerization is the most favorable reaction of $Co(NH_3)_5SCN^{2+}$.

Transition State for the Aquation of $Co(NH_3)_5NCS^{2+}$ or the Anation of $Co(NH_3)_5OH_2^{3+}$ by the N End of SCN^-. It was obtained by the above-described procedure. This transition state, $[Co(NH_3)_5\cdots(NCS)(OH_2)^{2+}]^{\ddagger}$ (Figure 10), has C_s symmetry.[23] It was calculated for the discussion of the anation of $Co(NH_3)_5OH_2^{3+}$ by SCN^- and for comparison with the two other transition states (of system 2). The imaginary mode, together with the bond length changes (Table 6), suggest also the I_d mechanism for this aquation. Interestingly, in this transition state $\sum d(Co{-}N(H_3))$ is the same as for the two others (Tables 5 and 6).

Discussion

The first-order rate constant for the two parallel reactions (1 and 2), the isomerization and the aquation, is $1.26 \times 10^{-6}\ s^{-1}$, and the $Co(NH_3)_5NCS^{2+}/Co(NH_3)_5OH_2^{3+}$ product ratio is 90.9:9.1 (25 °C and $I = 0.15$ M).[6] Therefore, the rate constants for reactions 1 and 2 are 1.15×10^{-6} and $1.1 \times 10^{-7}\ s^{-1}$, respectively. The corresponding free activation energies ($\Delta G_{298}^{\ddagger}$),

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(23) In this transition state, the Mulliken charge of the SCN^- ligand is −0.83. Therefore, the SCN^- *anion* is substituted.

calculated on the basis of the transition state theory (assuming that $\kappa = 1$), are reported in Tables 1 and 4.

Mechanism of the S → N Isomerization. The change of the sum of the Co−L bond lengths, $\Delta\sum d(\mathrm{Co-L})$, for this reaction (eq 1), calculated for the hydrated ions on the basis of systems 1 and 2, is 0.05 and 0.06 Å, and that for reaching the transition state is 0.06 and −0.02 Å (Tables 1 (i) and 4). For both systems, the computations yielded similar $\Delta\sum d(\mathrm{Co-L})$ values for the activation process and the overall reaction. This indicates that the *intrinsic* reaction volume for reaction 1 as well as the *intrinsic component* of the activation volume are small, close to zero. On the basis of this small change of $\Delta\sum d(\mathrm{Co-L})$, the I mechanism would be attributed to the S → N isomerization in water. In the transition state, the SCN^- ligand is more distant from the cobalt(III) center than in the reactant or product as shown by the $\sum d(\mathrm{Co-CNS})$ parameter (Tables 2 and 5). Since the (overall) $\Delta\sum d(\mathrm{Co-L})$ change to reach the transition state is small, the removal of the SCN^- group from the cobalt(III) center is compensated by the shrinkage of the $\mathrm{Co-N(H_3)}$ bonds (by 0.22 Å for both systems). The elongation of the Co···CNS bond during the activation lowers the electron density at the cobalt(III) center; its Mulliken charge increases by about 0.4. This reduction of electron density has been lessened partly by the shortening of the $\mathrm{Co-N(H_3)}$ bonds.

Alternatively, the trajectory of the SCN^- ligand alone might be considered: for the overall reaction, $\sum d(\mathrm{Co-CNS})$ increases slightly by 0.08 and 0.09 Å for the two systems (Tables 2 and 5), but the activation process involves a corresponding increase of 0.28 and 0.20 Å. This means that, in the transition state, the SCN^- ligand is appreciably more distant from the cobalt(III) center than in the reactant or product. If the motion of the SCN^- group alone is considered, the I_d mechanism would be attributed to the S → N isomerization.

We prefer the attribution of the I mechanism to the S → N isomerization on the basis of the $\Delta\sum d(\mathrm{Co-L})$ criterion, and this parameter should be comparable with the intrinsic component of the activation volume. The trajectory of the SCN^- ligand shows that, when this anion alone is considered, the isomerization is activated dissociatively, and this activation mode is observed generally in substitutions of amine complexes of cobalt(III). In the S → N isomerization, the elongation of the Co−SCN bond, $\Delta\sum d(\mathrm{Co-CNS})$, is relatively small, because the nucleophile, the N donor of SCN^-, is already close to the cobalt(III) center (Tables 2 and 5). For the aquation of $\mathrm{Co(NH_3)_5SCN^{2+}}$ and $\mathrm{Co(NH_3)_5NCS^{2+}}$, $\Delta\sum d(\mathrm{Co-CNS})$ is considerably larger (Table 6). The relatively small $\Delta\sum d(\mathrm{Co-CNS})$ value for the isomerization is compensated entirely by the shrinkage of the five $\mathrm{Co-N(H_3)}$ bonds. In the aquations, the $\mathrm{Co-N(H_3)}$ bonds are reduced to the same extent, but this reduction is smaller than the elongation of the Co−SCN and Co−NCS bonds, and therefore, the attribution of the I_d mechanism for reactions 2 and 3 is straightforward (see next section), whereas that for the isomerization depends on the choice of the criterion.

It is worthwhile to note that, in the transition state $[\mathrm{Co(NH_3)_5}\cdot\cdot\cdot\mathrm{CNS}\cdot\mathrm{OH_2}^{2+}]^\ddagger$, the water molecule in the second coordination sphere is closer to the cobalt(III) center by 0.05 Å than in the reactant or product (Table 5). This is due to the increased positive charge of cobalt(III) in the transition state. Correspondingly, the negative charge on the SCN^- ligand increases also during the activation, and the hydrogen bonds with SCN^- are expected to be strengthened, too. Therefore, all water molecules in the second coordination sphere are bound more strongly to the transition state, and this suggests that the *electrostrictive component* of the volume of activation is negative. The total volume of activation for the isomerization is therefore expected to be negative, since the intrinsic component is approximately zero (see above).

Table 7. Co···X and Co···Y Bond Lengths[a] in Transtion States $[\mathrm{Co(NH_3)_5}\cdot\cdot\cdot(\mathrm{X})(\mathrm{Y})^{n+}]^\ddagger$

reaction	d(Co···X), X	d(Co···Y), Y
S → N isomerization of $\mathrm{Co(NH_3)_5SCN^{2+}}$	3.48,[b] **S**CN 3.51,[c] **S**CN	3.20,[b] **N**CS 3.22,[c] **N**CS
aquation of $\mathrm{Co(NH_3)_5SCN^{2+}}$	3.94, **S**CN	3.13, **O**$\mathrm{H_2}$
aquation of $\mathrm{Co(NH_3)_5NCS^{2+}}$	3.05, **N**CS	2.84, **O**$\mathrm{H_2}$
aquation of $\mathrm{Co(NH_3)_5Cl^{2+}}$	3.47,[d] **Cl**	2.86,[d] **O**$\mathrm{H_2}$
water exchange of $\mathrm{Co(NH_3)_5OH_2^{3+}}$	3.37,[e,f] **O**$\mathrm{H_2}$	3.53,[e,f] **O**$\mathrm{H_2}$

[a] Units: angstroms. [b] System 2. [c] System 1. [d] Reference 11. [e] Reference 24. [f] Since this transition state has no symmetry, the two Co···O bonds are inequivalent.

The experimentally determined volume of activation, −5.3 ± 0.8 $\mathrm{cm^3/mol}$ at 50 °C and $I = 0.1$ M,[4] arises from both the isomerization and the aquation of $\mathrm{Co(NH_3)_5SCN^{2+}}$ (reactions 1 and 2). Since the contribution of each individual reaction is unknown, the computed $\Delta\sum d(\mathrm{Co-L})$ values cannot be compared with experiment.

Mechanism of the Aquations or Anations. The D and an interchange mechanism for the aquation of $\mathrm{Co(NH_3)_5SCN^{2+}}$ were investigated on the basis of systems 1 and 2, respectively. The interchange pathway requires a lower activation energy (Tables 1 (i) and 4) which is furthermore in agreement with experiment. Also the relative energy (ΔE) of the pentacoordinated intermediate $\mathrm{Co(NH_3)_5}\cdot\mathrm{SCN^{2+}}$ is higher than the activation energy for the concerted mechanism. Therefore, the D mechanism is very unlikely to be competitive with the interchange one.

The change of the sum of the Co−L bond lengths, $\Delta\sum d(\mathrm{Co-L})$, for reaction 2 is 1.07 Å. Since the $\Delta\sum d(\mathrm{Co-L})$ parameter for the activation process is much larger, namely, 1.84 Å, the attribution of the I_d mechanism for the aquation of $\mathrm{Co(NH_3)_5SCN^{2+}}$ and the corresponding anation is straightforward. The aquation of $\mathrm{Co(NH_3)_5NCS^{2+}}$ (as well as its inverse reaction) follows also the I_d mechanism, since $\Delta\sum d(\mathrm{Co-L})$ for the activation is even larger (2.07 Å). A general method for the determination of reaction mechanisms of asymmetric reactions based on bond length changes was described recently and applied to the aquations of $\mathrm{Co(NH_3)_5Cl^{2+}}$ and $\mathrm{Cr(NH_3)_5Cl^{2+}}$.[11]

Structure of the Transition States for the Isomerization and Aquation. The corresponding three transition states exhibit similar imaginary modes which describe the removal of the leaving group, the S end of SCN^- (Figures 5 and 8) or the N end of SCN^- (Figure 10). These processes occur concerted with the entry of the nucleophile, the N end of SCN^- (Figure 5) or H_2O (Figures 8 and 10). Also the positions of the entering and leaving *donor atoms* are roughly the same. The major differences between these transition states are the *pairs of involved donor atoms*, (S, N), (S, O), and (N, O). Furthermore, the transition states for the aquation of $\mathrm{Co(NH_3)_5Cl^{2+}}$ [11] and for the water exchange of $\mathrm{Co(NH_3)_5OH_2^{3+}}$ [24] (Table 7) are also similar to those shown in Figures 5, 8, and 10.

For the substitutions of X by Y in $\mathrm{Co(NH_3)_5X^{n+}}$ complexes, and also the isomerizations that are a special case thereof, the Co···X and Co···Y bond lengths are reported in Table 7. It should be noted that the length of the weak bonds depends on both the entering and the leaving group, and this is typical for the interchange mechanisms. Apart from the isomerization which

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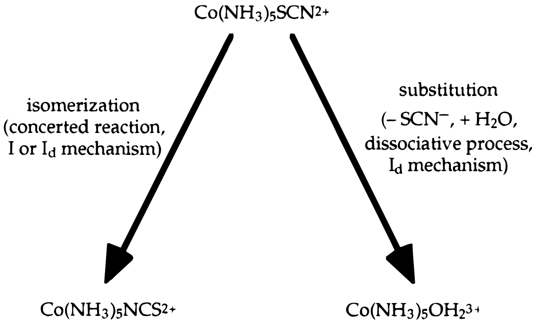
(24) Rotzinger, F. P. Work in progress.

Scheme 1



has already been discussed in the Results section and to which the I mechanism was attributed preferentially, all of these reactions follow the I_d mechanism (i) because there is no intermediate on the reaction paths, (ii) because the imaginary mode describes the removal of the leaving group that is concerted with the entry of the nucleophile, (iii) because the $\sum d(Co-L)$ values of the transition states are larger than those of the reactants or products, and (iv) because of the relatively long Co···X and Co···Y bonds. It should be noted that, in all reported transition states (Table 7), there is a significant contribution of bond formation. In these transition states, no reactant is located in the second coordination sphere, since the corresponding Co···X or Co···Y distances are considerably shorter than those when X or Y is in the second coordination sphere as in the reactant or product (Tables 5 and 6).

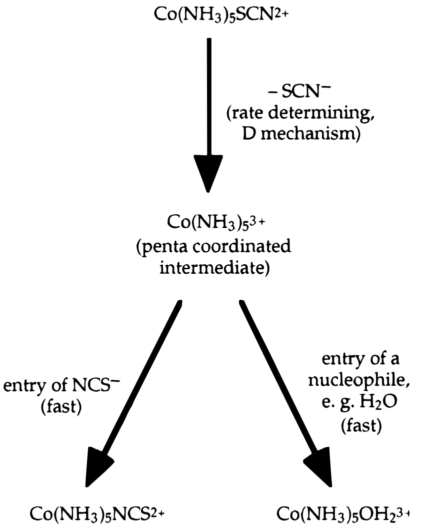
The SCN^- ligand could also be substituted by nucleophiles like $S^{14}CN^-$,[6] N_3^-, or others. The corresponding transition states would resemble that of $[Co(NH_3)_5\cdots(SCN)(OH_2)^{2+}]^\ddagger$ with the donor atom of the entering group at about the same location as the oxygen atom of water.

Mechanism of the Reactions of $Co(NH_3)_5SCN^{2+}$ in Aqueous Solution. The common feature of the isomerization and aquation (reactions 1 and 2) is the weakening of the Co−S bond. For the isomerization, it is concerted with the entry of the N end of SCN^-, whereas for the aquation, the O donor atom of water approaches the cobalt(III) center also in a concerted manner. The present calculations indicate that reactions 1 and 2 are *parallel events* (Scheme 1) that involve *two disparate transition states* (Figures 5 and 8). As described above, they exhibit some similarities.

The alternative reaction mechanism, represented in Scheme 2, is inconsistent with experiment and the present computational results. It would involve a rate-determining breaking of the Co−S bond that would lead to the short-lived pentacoordinated intermediate $Co(NH_3)_5{\cdot}SCN^{2+}$, which would react subsequently with either the N donor of SCN^- or water. As already mentioned in the Introduction, the small, but positive, volumes of activation for the substitution of neutral leaving groups in $Co(NH_3)_5X^{3+}$ complexes supply strong evidence for the I_d mechanism.[3] According to the presently calculated activation energies (Tables 1 (i) and 4), the I_d pathway is also more advantageous for the aquation of $Co(NH_3)_5SCN^{2+}$ than the SCN^- substitution via the D mechanism (Tables 1 (i) and 4).

Role of the Nucleophile and Leaving Group in Substitutions on Pentaamine Complexes of Cobalt(III). The aquation of both $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ follows the I_d mechanism. Since the latter product is more stable, the N donor of SCN^- is a better nucleophile than the S donor. Although in the transition states $[Co(NH_3)_5\cdots(NCS)(OH_2)^{2+}]^\ddagger$ and $[Co(NH_3)_5\cdots(SCN)(OH_2)^{2+}]^\ddagger$ the Co···N and Co···S bonds are weak, the calculated total energy of the former is lower by 4.3 kJ/mol. The more nucleophilic site of SCN^- gives rise to a slightly more stable transition state. The typical feature of the I_d mechanism is the larger extent of bond breaking compared with bond making. The small, but significant, energy difference of 4.3 kJ/mol reflects the better nucleophilicity of the N donor of SCN^-.

Scheme 2



The anation of $Co(NH_3)_5OH_2^{3+}$ by SCN^- also follows the I_d mechanism, because of the microscopic reversibility. The formation of $Co(NH_3)_5NCS^{2+}$ is favorable, and on the basis of kinetic data,[6] a difference in activation energies of 3 kJ/mol is estimated for the formation of $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5SCN^{2+}$. Since the ion-pairing constant is the same for the two anations, this *difference* in activation energies reflects the relative stabilities of the two transition states $[Co(NH_3)_5\cdots(NCS)(OH_2)^{2+}]^\ddagger$ and $[Co(NH_3)_5\cdots(SCN)(OH_2)^{2+}]^\ddagger$. The calculated 4.3 kJ/mol is in perfect agreement with experiment.

Conclusions

The present calculations indicate the following: (i) The S → N isomerization of $Co(NH_3)_5SCN^{2+}$ follows an interchange mechanism (I or I_d), since it proceeds in a single step and does not involve any intermediate. (ii) The T-shaped species that had already been postulated in the very first study[5] of the S → N isomerization reaction exists. It is a transition state and not, for example, an intermediate. (iii) The aquation of $Co(NH_3)_5SCN^{2+}$ (and probably also the substitutions of SCN^- by other nucleophiles) follows the I_d mechanism. (iv) Isomerization and aquation of $Co(NH_3)_5SCN^{2+}$ are parallel reactions which proceed via disparate transition states. (v) For both the isomerization and the aquation, the D mechanism is not competitive. (vi) The anation of $Co(NH_3)_5OH_2^{3+}$ by the N or S end of SCN^- follows also the I_d mechanism. The transition state, in which the more nucleophilic N site of SCN^- is involved, is slightly more stable. This shows that, for the I_d mechanism, the extent of bond making is relevant.

Computational Details

All of the calculations were performed on Cray T3D, Cray Y-MP/M94, HP 9000/735, and HP 9000/C200 computers using the GAMESS[25] program.

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[25] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

The basis sets of Stevens, Basch, Krauss, and Jasien[26] were used for cobalt, 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 shell has triple-ζ quality. For sulfur, the basis sets of Stevens, Basch, and Krauss,[27] supplemented with a 3d polarization function, were employed ($\alpha_{3d}(S) = 0.55$[28]). For C, N, O, and H, 6-31G-(d) basis sets[29,30] were used ($\alpha_{3d}(C) = 0.80$,[28] $\alpha_{3d}(N) = 1.00$,[28] $\alpha_{3d}(O) = 1.20$[28]).

For the SCRF calculations,[12-14] the cavity radius was taken as half of the value of the largest interatomic distance plus the two corresponding van der Waals radii. Once the geometry had converged, the cavity radius was redetermined, and if it differed by more than 0.01 Å from the previous value, the geometry optimization was repeated until the above criterion was fulfilled.

The active space for the CAS-SCF calculation was determined using the iterative natural orbital (INO) method.[21] First, the three d_π levels of cobalt(III) and the six highest molecular orbitals were correlated with the entire virtual space using singles-doubles CI calculations. The 12 natural orbitals with occupations greater than 0.01 and smaller than 1.99 were kept and constituted the large active space for the transition state search at the CAS-SCF level.

Acknowledgment. The “Service informatique central” is acknowledged for computer time on the Cray T3D and Y-MP/M94 computers and Dr. R. Humphry-Baker for proof-reading of the manuscript. Professor Dr. D. A. Buckingham contributed helpful comments.

Supporting Information Available: Tables listing the atomic coordinates of all hydrated ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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