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The Cause for Tremendous Acceleration of Chloride Substitution via Base Catalysis in the Chloro Pentaammine Cobalt(III) Ion

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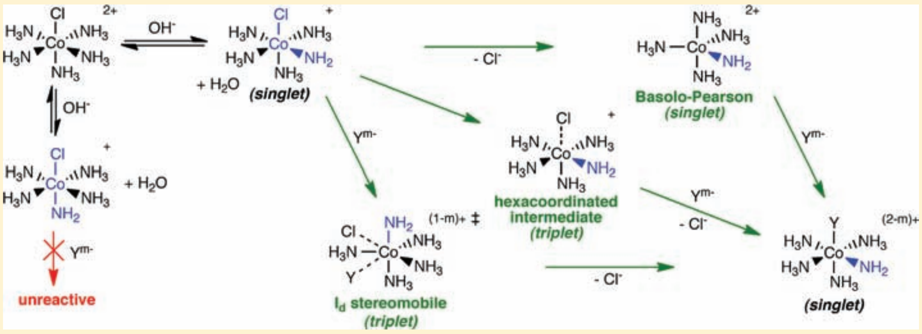
Supporting Information

ABSTRACT:



The base hydrolysis reaction of $Co(NH_3)_5Cl^{2+}$ was investigated using density functional theory and molecular orbital methods. Geometries and energies of conjugate bases, intermediates, transition states, and minimum energy crossing points were computed. For the base hydrolysis of $Co(NH_3)_5Cl^{2+}$, three pathways might operate: the mechanism proposed by Basolo and Pearson, the mechanism via a hexacoordinated intermediate exhibiting a triplet ground state, and a fully stereomobile I_d mechanism. The hexacoordinated intermediate can lose the leaving ligand readily to form a square pyramidal pentacoordinated intermediate with a triplet state, which interconverts rapidly and reversibly into the Basolo—Pearson trigonal bipyramid with a singlet state. Due to its high activation energy, a stereochemical rearrangement via a Berry pseudorotation does not take place. The intermediates are not protonated because their pK_a values are ~5 for the hexacoordinated intermediate and ~−6 for the trigonal bipyramidal pentacoordinated intermediate. The Basolo—Pearson mechanism proceeds with 50% stereoretention and 50% stereomobility. In the case that the hexacoordinated intermediate converts into the trigonal bipyramid, products with the same stereochemistry would be obtained. If, however, for the square pyramidal intermediate with a triplet state the entering ligand competes efficiently with the rearrangement into the trigonal bipyramid or if the substitution takes place at the hexacoordinated intermediate via, e.g., the I_d mechanism, the reaction would proceed with retention of the configuration. Direct substitution via the I_d mechanism, operating for azide and to a small extent also for water, is fully stereomobile. Computations on the Basolo—Pearson mechanism have also been performed for the chloro pentaammine complexes of chromium(III), ruthenium(III), and rhodium(III). This pathway might operate for chromium(III) but not for ruthenium(III) and rhodium(III).

INTRODUCTION

Base-catalyzed substitution reactions of amine complexes of cobalt(III) were studied extensively[1−3] for mainly two reasons. First, was the quest of the proof for the presence or absence of a pentacoordinated intermediate in the course of such reactions. The second motivation dealt with the elucidation of the cause of the tremendous acceleration arising from deprotonation of an amine ligand cis to the leaving ligand. Experimental evidence for the existence of hexacoordinated intermediates in the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ (X^{n-} = DMSO, NO_3^-, SO_4^{2-}) was presented[4,5] 20 years ago. A few years later, pentacoordinated intermediates were detected experimentally in reactions of $Co(NH_2CH_3)_5X^{(3-n)+}$ (X^{n-} = DMF, Cl^-)[6] and Co(*mer*-triamine)(diamine)Cl^{2+} complexes.[7,8] In a qualitative quantum chemical study based on modified extended Hückel and SCF MS-Xα calculations, it was suggested that the unique reactivity of ammine complexes of cobalt(III), deprotonated cis to the leaving ligand, could be due to the existence of (deprotonated) hexacoordinated intermediates exhibiting a low-lying triplet ground state.[9] This finding corroborated the experimentally inferred[4,5] hexacoordinated intermediates *cis*-$Co(NH_3)_4(NH_2)\cdots X^{(2-n)+}$.

In the present study, quantum chemical computations on the base hydrolysis reaction of the experimentally well-characterized $Co(NH_3)_5Cl^{2+}$ ion[10−13] were performed to assess the origin of the high reactivity of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ and answer the question of the presence of intermediates.

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As nucleophiles, H_2O and N_3^- were investigated; Green and Taube[14,15] have shown based on ^{18}O-labeling experiments that H_2O and not OH^- is the entering ligand in the base hydrolysis of $Co(NH_3)_5X^{2+}$ (X = Cl, Br, NO_3).

The conjugate base mechanism was first proposed by Garrick[16] in 1937. About 20 years later, Basolo and Pearson[17] raised the hypothesis that the high reactivity of the conjugate base arises from the stabilization of the trigonal bipyramidal pentacoordinated intermediate $Co(NH_2)(NH_3)_4^{2+}$ via π donation of the amido lone pair into the empty $d_{x^2-y^2}$ molecular orbital (MO) of cobalt(III). The electronic state of this species would be a singlet. As it will be shown in this study, this pathway has indeed a much lower activation energy than that involving the conjugate base *trans*-$Co(NH_3)_4(NH_2)Cl^+$. Basolo and Pearson's hypothesis[17] stimulated a large number of experimental studies, which were devoted to proof of the existence or nonexistence of a pentacoordinated intermediate in the course of this reaction.

In 1967, Gillard[18] attributed the high reactivity of the base-catalyzed pathway to a redox process in which OH^- reduces the inert cobalt(III) center to labile cobalt(II). This reaction is expected to be thermodynamically less favorable than an "internal redox process" involving reduction of cobalt(III) by the deprotonated amine ligand within the conjugate base. Such a mechanism has been mentioned in passing by Buckingham, Marty, and Sargeson.[19] It would involve the low-spin *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})Cl^+$ species, which was also investigated in the present work.

Alternatively, the unexpectedly high reactivity of the conjugate base was proposed[9] to arise from an energetically low-lying hexacoordinated intermediate exhibiting a triplet ground state. Such a pathway, proceeding via the minimum energy crossing point (MECP) between the singlet potential energy surface (PES) of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ and the triplet PES of the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$, has also been investigated. Other mechanisms involving species with quintet states have also been studied.

The stereochemistry of the base hydrolysis of *trans*-$Co(NH_3)_4(^{15}NH_3)X^{(3-n)+}$ complexes[20] cannot be rationalized on the basis of Basolo and Pearson's[17] mechanism or the pathway[4,5,9] involving a hexacoordinated intermediate. For this reason, an additional concerted mechanism proceeding via *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(Y)^{(1-m)+\ddagger}$ (Y^{m-}: H_2O, N_3^-, OH^-) transition states with a triplet electron configuration were investigated. (The tightly bound NH_2^- and NH_3 ligands form a trigonal bipyramid with NH_2^- in the axial position.)

For chromium(III), ruthenium(III), and rhodium(III), the pathway via the hexacoordinated intermediate exhibits a high activation energy.[9] The Basolo–Pearson mechanism,[17] which has not been computed so far for these transition metal complexes, was studied as well.

COMPUTATIONAL DETAILS

Calculations were performed using the GAMESS[21,22] programs. For cobalt, chromium, ruthenium, and rhodium the relativistic effective core potential (ECP) basis sets of Stevens et al. (SBKJC)[23] were used. For chlorine, the ECP basis set of Stevens et al.[24] supplemented with a polarization function ($\alpha_d = 0.65^{25}$) was taken. For N and H, the 6-31G(d) basis set[26,27] was used ($\alpha_d = 1.00^{25}$). Figures 1–5, 7, 8, and S1–S14, Supporting Information, were generated with MacMolPlt.[28]

Hydration was treated using the conductor polarizable continuum model (CPCM).[29–31] The cavity was constructed based on the van der Waals radii of the atoms, whereby for cobalt, chromium, ruthenium, and rhodium values of 2.20, 2.20, 2.30, and 2.30 Å, respectively, were taken. Because of the high oxidation state of the metals in these complexes, a finer tessellation than the default had to be used (NTSALL=960 and MTHALL=2, the respective defaults are 60 and 4). Geometries and energies were computed with density functional theory (DFT) using the OPBE functional,[32–34] which is based on the OPTX exchange.[34] This functional provides acceptable doublet–quartet, singlet–triplet, and singlet–quintet energy differences.[35,36] It should be noted that for computation of the two minimum energy crossing points (MECP), a functional yielding an accurate singlet–triplet energy difference is required (see below). The DFT calculations were performed with a grid finer (NTHE=24 and NPHI=48) than the default (NTHE=12 and NPHI=24). The adequacy of the OPBE energies was established by high-level wave function theory, multiconfiguration quasi-degenerate second-order perturbation (MCQDPT2)[37,38] theory, which was applied to the key species. The active space for the MCQDPT2 computations was determined via configuration interaction (CI) singles–doubles

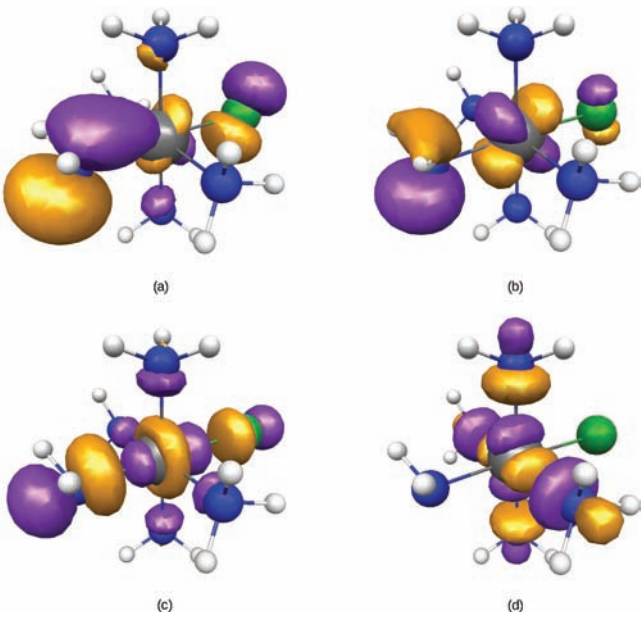


Figure 1. Important OPBE MOs of the conjugate base *trans*-$Co(NH_3)_4(NH_2)Cl^+$: (a) $\pi(d_\pi(Co)-p_\pi(NH_2^-))$, (b) $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$, (c) $d_\sigma^*(Co-Cl)$, and (d) d_σ^*.

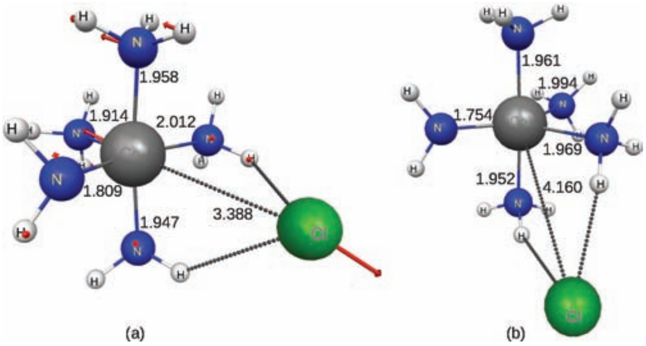


Figure 2. (a) Perspective view, imaginary mode (70*i* cm^{-1}), and cobalt(III)–ligand bond lengths (Å) of the transition state *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ for the mechanism postulated[17] by Basolo and Pearson (singlet state). (b) Perspective view of the corresponding trigonal bipyramidal pentacoordinated intermediate *cis-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$.

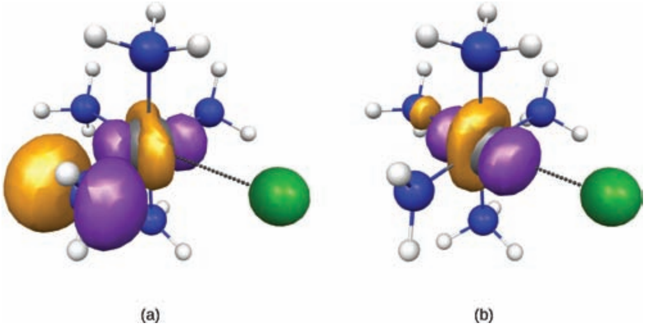


Figure 3. Singly occupied CAS-SCF(10/10) natural orbitals of the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$: (a) $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$, populated by 1.0637 electrons, and (b) $d_\sigma^*(Co-Cl)$, populated by 1.0185 electrons.

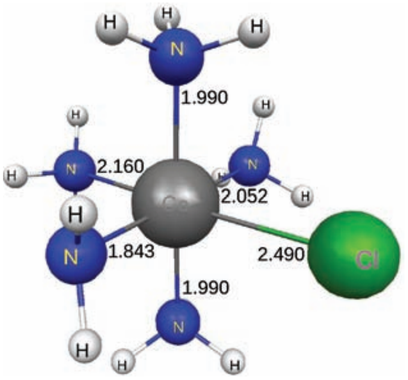


Figure 4. Perspective view and cobalt(III)−ligand bond lengths (Å) of the transition state *cis*-$Co(NH_3)_4(NH_2)Cl^{+\ddagger}$ (MECP).

calculations.[39] A 10 electrons in 10 orbitals (10/10) active space was used for all MCQDPT2 calculations. Hydration at the MCQDPT2 level was computed as described.[40] Unless noted otherwise, only the 1s MOs of N were treated as frozen cores. Zero-point energies and thermal corrections were not included; this is anyway not possible for MECPs.

The transition states *cis*- and *trans*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (singlet states), *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (triplet state), $Co(NH_3)_4(NH_2)^{2+\ddagger}$, *ap-sqp*-$Co(NH_3)_4(NH_2)^{2+\ddagger}$, *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^{\ddagger}$ (triplet state), *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH_2)^{+\ddagger}$ (triplet state), *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH)^{\ddagger}$ (triplet state), *cis*-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$, and $Cr(NH_3)_5\cdots Cl(OH)^{+\ddagger}$ were located by maximizing the energy along the reaction coordinate (the imaginary mode) via Eigen-mode following. The Hessians were calculated numerically (based on analytical gradients) using the double-difference method and projected to eliminate rotational and translational contaminants.[41]

The geometry of the MECP connecting the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ (exhibiting a singlet ground state) and the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (exhibiting a triplet ground state) and that between *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ (singlet state) and *bas-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ (triplet state) was computed at the OPBE level (with CPCM hydration). The OPBE calculations on the triplet (and quintet) states were performed at the spin-unrestricted level. The singlet and triplet energies of these MECPs were furthermore computed with MCQDPT2-(10/10) (including CPCM hydration), whereby the singlet energy is higher by 4.1 kJ/mol for *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ and lower by 8.6 kJ/mol for $Co(NH_3)_4(NH_2)^{2+\ddagger}$. Thus, OPBE and MCQDPT2(10/10) energies agree. Spin−orbit (SO) coupling of the MECP *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ was obtained in two ways: first, the CAS-SCF(10/10) MOs of the singlet state were computed, and for the triplet, the CAS-SCF(10/10) MOs were calculated with MOs 1−31 of the singlet kept frozen; only the MOs of the (10/10) active space were optimized for the triplet. On the basis of these two sets of MOs, SO splitting was computed via SO-CI(10/10); the splitting energy is 111 cm^{-1}. In the second SO-CI(10/10) calculation, the (fully optimized) CAS-SCF(10/10) MOs of the triplet together with the partially optimized CAS-SCF(10/10) MOs of the singlet (exhibiting MOs 1−31 of the triplet) were taken. This splitting energy is smaller, 41 cm^{-1}. A SO-CI calculation with fully optimized MOs of the singlet and triplet states is prohibitive. Thus, the singlet−triplet splitting energy of the MECP is in the range of 41−111 cm^{-1}. The SO-CI computations were based on the full Breit−Pauli Hamiltonian including a partial two-electron operator.[42−44] The atomic coordinates of all of the investigated species are given in Tables S3−S41 (Supporting Information).

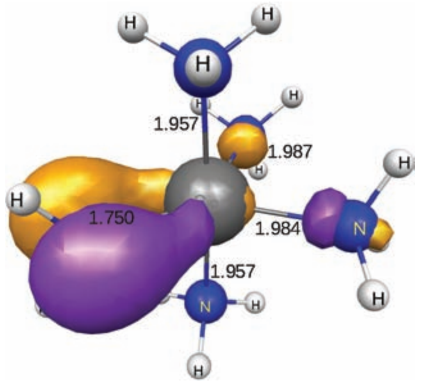
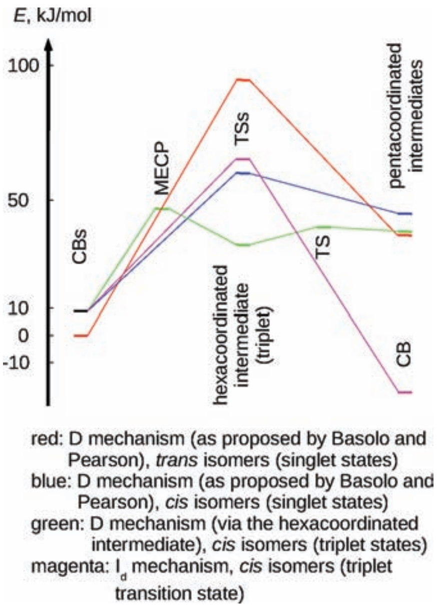


Figure 5. Perspective view, cobalt(III)−ligand bond lengths (Å), and MO 29 of the trigonal bipyramidal pentacoordinated intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$, postulated[17] by Basolo and Pearson (singlet state).

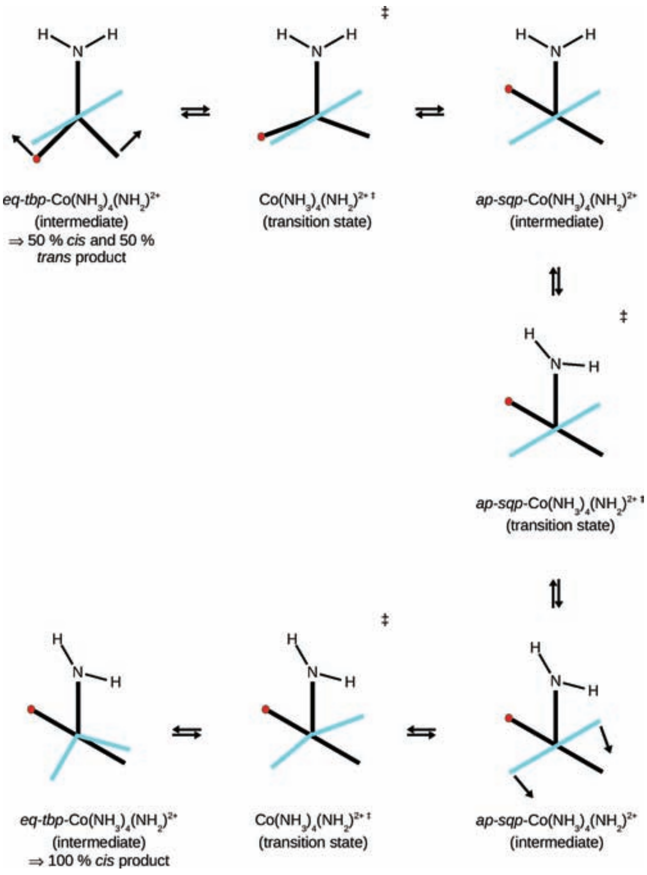
Scheme 1



■ RESULTS

Investigated Substitution and Rearrangement Mechanisms. Four pathways for substitution of the chloride leaving

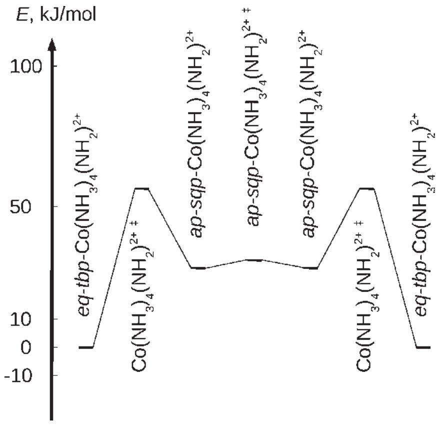
Scheme 2



group were computed (Scheme 1): the mechanism introduced by Basolo and Pearson[17] for the cis and trans isomers of the conjugate base, the mechanism proceeding via the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$,[4,5,9] and a concerted mechanism involving transition states with a triplet state. The first two pathways lead to the trigonal bipyramidal pentacoordinated intermediate *cis*- or *trans*-*eq*-*tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (Cl^- is approximately cis or trans to NH_2^-) with the chloride ion in the second coordination sphere. In the third pathway, the hexacoordinated intermediate looses the weakly bound chloride ligand in a consecutive reaction via the D mechanism (Scheme 1), which leads to a square pyramidal pentacoordinated intermediate *bas*-*sqp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (with NH_2^- in the basal plane and Cl^- in the second coordination sphere). Rearrangement of the trigonal bipyramidal pentacoordinated intermediate *eq*-*tbp*-$Co(NH_3)_4(NH_2)^{2+}$ (with NH_2^- in the trigonal plane) exhibiting a singlet ground state into square pyramidal *bas*-*sqp*-$Co(NH_3)_4(NH_2)^{2+}$ with a triplet ground state proceeds via a single MECP. Rearrangement of *eq*-*tbp*-$Co(NH_3)_4(NH_2)^{2+}$ via Berry pseudorotation is not competitive with nucleophile addition, since it involves two transition states and the energetically high-lying square pyramidal pentacoordinated intermediate *ap*-*sqp*-$Co(NH_3)_4(NH_2)^{2+}$ with the NH_2^- ligand in the apical position (Schemes 2 and 3).

As mentioned in the Introduction, the above-presented mechanisms cannot account for the stereochemistry of the base hydrolysis of *trans*-$Co(NH_3)_4(^{15}NH_3)X^{(3-n)+}$ complexes:[20] the Basolo–Pearson mechanism would lead to products with exactly 50% cis and 50% trans configurations, whereas the pathway via the hexacoordinated intermediate would yield ≤50% cis and ≥50% trans. Neither pathway can account for >50% cis product. Therefore, an additional fourth pathway giving rise to stereomobility had to be found. Among many trials, computation of the transition states *ax*-*tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^‡$ and *ax*-*tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH_2)^{+‡}$ exhibiting triplet ground states was successful. In the presence of N_3^- and H_2O, reactions via this pathway are feasible and 100% stereomobile.

Scheme 3



Finally, the "internal redox mechanism"[19] was investigated, together with pathways involving intermediates with quintet and triplet states.

The total and the relative energies of all computed species are given in Tables 1 and S1, Supporting Information. Pertinent vertical transition energies are reported in Table 2.

Validation of the Model and the Computational Method. The Co–N bond lengths in a variety of $Co(NH_3)_6^{3+}$ salts can be reproduced by quantum chemical computations[36] based on the OPBE functional,[32–34] provided that the environment of the $Co(NH_3)_6^{3+}$ cation is modeled by 4 Cl^- anions in a pseudotetrahedral arrangement or that the cation is hydrated via the polarizable continuum model (PCM).[29,30] The energies of all of the key species were also computed with MCQDPT2[37,38] (Table S1, Supporting Information), and the corresponding OPBE energy differences deviate by less than 15 kJ/mol (in most cases by <5 kJ/mol) for reactions with and without spin changes (Table 1). This shows that the OPBE functional produces accurate geometries and energy differences between states with different spin multiplicities for the presently studied ammine complexes of cobalt(III).

The geometry of $Co(NH_3)_5Cl^{2+}$ was optimized at the OPBE level, whereby hydration was modeled with the conductor polarizable continuum model (CPCM).[29–31] Two X-ray crystal structures, with hexafluoro silicate[45] and chloride[46] as counterions, are available (Table S2, Supporting Information). For the SiF_6^{2-} salt, the cobalt(III)–ligand bond lengths are longer and their standard deviations are larger. The longer bonds as well as their larger error limits might be due to the rather strong F···H bonds. The computed metal–ligand bond lengths (Table S2, Supporting Information) agree with those of the chloride salt, $[Co(NH_3)_5Cl]Cl_2$. No trans effect is seen in the $[Co(NH_3)_5Cl]Cl_2$ crystal, presumably because of the hydrogen bonds, which weaken the Co–Cl bond (via acceptance of charge by NH_3 of neighboring cations) and strengthen the Co–N bonds (via donation of charge by Cl^-). The water solvent exerts a similar effect onto the $Co(NH_3)_5Cl^{2+}$ ion because the CPCM model takes

Table 1. Reaction (ΔE) and Activation ($\Delta E^{\ddagger}$) Energies

reaction[a]	ΔE or $\Delta E^{\ddagger}$, kJ/mol	
	OPBE	MCQDPT2
(i) isomerization of the conjugate bases		
trans-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Co(NH_3)_4(NH_2)Cl^+$ (CB)	9.0	11.6
(ii) substitution via the D mechanism and singlet states		
cis-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)	51.1	44.3
cis-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (INT)	36.1	35.7
cis-eq-tbp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (INT) → *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)	15.1	8.6
trans-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *trans*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)	94.6	97.6
trans-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *trans-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (INT)	37.0	34.1
trans-eq-tbp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (INT) → *trans*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)	57.7	63.4
(iii) substitution via the D mechanism and triplet states		
cis-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Co(NH_3)_4(NH_2)Cl^{+\ddagger}$ (MECP)	37.8	37.3
cis-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (INT)[b,d]	24.4	23.1
cis-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (INT)[b,d] → *cis*-$Co(NH_3)_4(NH_2)Cl^{+\ddagger}$ (MECP)	13.4	14.2
cis-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (INT)[b,d] → *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)[b]	6.6	6.2
cis-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (INT)[b,d] → *cis-bas-sqp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (INT)[b]	5.1	4.3
cis-bas-sqp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (INT)[b] → *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)[b]	1.4	1.9
(iv) rearrangements		
eq-tbp-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[e] → $Co(NH_3)_4(NH_2)^{2+\ddagger}$ (MECP)	10.1	8.2
eq-tbp-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[e] → *bas-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[b]	−3.9	6.4
bas-sqp-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[b] → $Co(NH_3)_4(NH_2)^{2+\ddagger}$ (MECP)	14.0	1.8
eq-tbp-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[e] → $Co(NH_3)_4(NH_2)^{2+\ddagger}$ (TS)[e]	56.4	53.6
eq-tbp-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[e] → *ap-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[e]	28.2	27.6
ap-sqp-$Co(NH_3)_4(NH_2)^{2+}$ (INT)[e] → *ap-sqp*-$Co(NH_3)_4(NH_2)^{2+\ddagger}$ (TS)[e]	2.9	3.7
(v) stereomobile substitution via the I_d mechanism and triplet states		
cis-$Co(NH_3)_4(NH_2)Cl\cdot N_3$ → *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^{\ddagger}$ (TS)[b]	56.3	
cis-$Co(NH_3)_4(NH_2)Cl\cdot N_3$ → *cis*-$Co(NH_3)_4(NH_2)N_3\cdot Cl$	−29.9	
cis-$Co(NH_3)_4(NH_2)Cl\cdot OH_2^+$ → *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH_2)^{+\ddagger}$ (TS)[b]	59.2	
(vi) mechanisms involving other intermediates with triplet or quintet states		
cis-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl^+$ (CT)[b]	176.6	
cis-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Co(NH_3)_4(NH_2)Cl^+$ (INT)[c]	66.3	
trans-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (INT)[b]	46.3	
trans-$Co(NH_3)_4(NH_2)Cl^+$ (CB) → *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (INT)[c]	73.5	
(vii) base hydrolysis of chloro pentaammine complexes of Cr(III), Ru(III), and Rh(III) via the Basolo−Pearson mechanism		
cis-$Cr(NH_3)_4(NH_2)Cl^+$ (CB) → *cis*-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)	43.6	
cis-$Cr(NH_3)_4(NH_2)Cl^+$ (CB) → *cis-eq-tbp*-$Cr(NH_3)_4(NH_2)\cdot Cl^+$ (INT)	32.1	
cis-eq-tbp-$Cr(NH_3)_4(NH_2)\cdot Cl^+$ (INT) → *cis*-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (TS)	11.5	
cis-$Ru(NH_3)_4(NH_2)Cl^+$ (CB) → *cis-eq-tbp*-$Ru(NH_3)_4(NH_2)\cdot Cl^+$ (INT)	76.5	
cis-$Rh(NH_3)_4(NH_2)Cl^+$ (CB) → *cis-eq-tbp*-$Rh(NH_3)_4(NH_2)\cdot Cl^+$ (INT)	72.7	
(viii) chloride substitution in chloro pentaammine chromium(III) by hydroxide via the I_a mechanism		
$Cr(NH_3)_5Cl\cdot OH^+$ → $Cr(NH_3)_5\cdots Cl(OH)^{+\ddagger}$	99.6	
$Cr(NH_3)_5Cl\cdot OH^+$ → $Cr(NH_3)_5OH\cdot Cl^+$	−73.6	

[a] Abbreviations: CB, conjugate base; INT, intermediate; TS, transition state; MECP, minimum energy crossing point; CT, charge transfer state. [b] Triplet state. [c] Quintet state. [d] Hexacoordinated intermediate. [e] Singlet state.

into account electrostatic interactions, the major effects of hydrogen bonding, but not the directionality of the H bonds. H bonding in ammine complexes is weaker than in aqua complexes due to the higher pK_a values of the former.

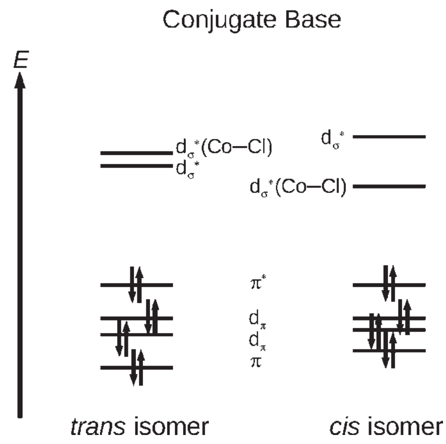
It should be noted that the singlet−triplet and singlet−quintet energy differences are very sensitive to the crystal field splitting parameter Δ.[36] To obtain an accurate Δ, the geometry and environment of the cation have to be modeled adequately.[36] The presently used OPBE functional and CPCM hydration yield sufficiently accurate geometries (Table S2, Supporting Information) and energy differences (Table 1). More sophisticated solvation methods are available,[47] but they are not applicable for the present systems.

Table 2. Vertical Transition Energies (ΔE)

excited state	remarks	ΔE,[a] kJ/mol
	(i) *trans*-$Co(NH_3)_4(NH_2)Cl^+$, conjugate base, singlet ground state	
first triplet		120.5
higher excited triplet[b]		149.9
first excited quintet		205.3
	(ii) *cis*-$Co(NH_3)_4(NH_2)Cl^+$, conjugate base, singlet ground state	
first excited triplet		98.4
higher excited triplet	charge transfer state *cis*-$Co^{II}(NH_3)_4(NH_2^•)\cdots Cl^+$	289.6
first excited quintet		207.7
	(iii) *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$, hexacoordinated intermediate, triplet ground state	
first excited singlet state		70.6
	(iv) *cis*-$Co(NH_3)_4(NH_2)\cdot Cl^+$, trigonal bipyramidal pentacoordinated intermediate, singlet ground state	
first excited triplet state		35.8

[a] OPBE energies. [b] Transition of a $\pi^*(d_\pi(Co)-p_\pi^*(NH_2^-))$ electron into the $d_\sigma^*(Co-Cl)$ MO (Scheme 4).

Scheme 4



Conjugate Base *trans*-$Co(NH_3)_4(NH_2)Cl^+$. In *trans*-$Co(NH_3)_4(NH_2)Cl^+$, formed via deprotonation of the trans NH_3 ligand in $Co(NH_3)_5Cl^{2+}$, the Co–Cl bond is elongated by ~0.1 Å (Table S2 and Figure S1, Supporting Information). The amido ligand is a p_π donor and a stronger σ donor than NH_3 as manifested by the shortened $Co-N(H_2)$ bond. The $Co-N(H_3)$ bonds do not alter significantly upon deprotonation. The p_π lone pair of the pyramidal NH_2^- ligand interacts with the corresponding d_π (t_{2g}-type) molecular orbital (MO) of cobalt(III) yielding a bonding $\pi(d_\pi(Co)-p_\pi(NH_2^-))$ MO (Figure 1a) and an antibonding $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$ MO (Figure 1b), which are both populated by 2 electrons (Scheme 4). The $d_\sigma^*(Co-Cl)$ (e_g^*-type) MO (Figure 1c) exhibiting electron density in the $H_2N-Co-Cl$ axis lies above the d_σ^* level, being antibonding with respect to the four NH_3 ligands (Figure 1d). The lowest vertical singlet–triplet excitations into these two d_σ^* levels (Table 2) involve excitation of a $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$ electron. In the (vertical) singlet–quintet transition, each d_σ^* MO is populated by one electron, whereby the second electron arises from the higher of the two $d_\pi(Co)$ levels (Scheme 4).

Conjugate Base *cis*-$Co(NH_3)_4(NH_2)Cl^+$. Its energy is higher by ~10 kJ/mol than that of the trans isomer (Table 1). The $Co-N(H_3)$ bond trans to the (pyramidal) NH_2^- ligand is elongated by ~0.08 Å, whereas the Co–Cl bond length is only slightly longer than that in the reactant $Co(NH_3)_5Cl^{2+}$ (Table S2 and Figure S2, Supporting Information). The ground state geometry of this conjugate base does not reveal its higher reactivity, in contrast to the trans isomer (which exhibits a longer Co–Cl bond). The MO diagram (Scheme 4) gives a clue why the cis conjugate base could be more reactive for the pathway via the hexacoordinated intermediate: in contrast to the trans isomer, the $d_\sigma^*(Co-Cl)$ MO is lower than d_σ^* and the HOMO–LUMO gap is smaller. The vertical singlet–triplet transition, in which a $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$ electron is promoted into the $d_\sigma^*(Co-Cl)$ level, requires a considerably lower energy (by ~50 kJ/mol) than for the trans isomer (Table 2). Furthermore, population of the $d_\sigma^*(Co-Cl)$ MO will weaken the Co–Cl bond. The origin of the low activation energy for the Basolo–Pearson mechanism cannot be seen in the ground state geometry and electronic structure of this conjugate base but is evident from the electronic structure of the trigonal bipyramidal pentacoordinated intermediate.[17]

Substitution Reaction of the Conjugate Base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ via the D Mechanism As Proposed by Basolo and Pearson. This is the mechanism that had been introduced in 1956.[17] In the transition state *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ the $Co\cdots Cl$ bond is elongated considerably (Figure 2a). Interestingly, the reaction coordinate (the imaginary mode) describes solely the severance of the $Co\cdots Cl$ bond; the rearrangement of the square pyramid into the trigonal bipyramid takes place afterward. Also, the stabilization of the p_π MO of NH_2^- cannot be seen in the transition state because the trigonal bipyramid is not formed at this stage; the $p_\pi(NH_2^-)$ MO still forms the π and π^* MOs as illustrated in the conjugate base *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (Figure 1a and 1b). It should be noted that although formation of the trigonal bipyramid and stabilization of $p_\pi(NH_2^-)$ cannot be seen in the transition state, the activation energy for Cl^- elimination in *cis*-$Co(NH_3)_4(NH_2)Cl^+$ of ~44–51 kJ/mol (Table 1, Scheme 1) is about one-half of that for the aquation of $Co(NH_3)_5Cl^{2+}$.[10,11,13,48] Rearrangement of the square pyramidal transition state leads to Basolo and Pearson's trigonal bipyramidal pentacoordinated intermediate *cis-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (Figure 2b, *eq* means that NH_2^- is in the equatorial plane, and Cl^- in the second coordination sphere is cis to NH_2^-).[17]

Substitution Reaction of the Conjugate Base *trans*-Co$(NH_3)_4(NH_2)Cl^+$ via the D Mechanism. Due to the presence of a strong donor (NH_2^-) trans to the leaving ligand (Cl^-) exerting a strong trans influence, this reaction might be expected to be even faster than that of (the conjugate base) *cis*-Co$(NH_3)_4(NH_2)Cl^+$. The computations, however, indicate that this pathway has a high activation energy (Table 1, Scheme 1). This reaction is only slightly more facile than the aquation of the nondeprotonated reactant $Co(NH_3)_5Cl^{2+}$.[10,11,13,48] The corresponding trigonal bipyramidal pentacoordinated intermediate *trans-eq-tbp*-Co$(NH_3)_4(NH_2)\cdot Cl^+$ has approximately the same energy as that formed from the cis conjugate base because these two species differ only in the position of Cl^- located in the second coordination sphere. The activation energy for the reverse reaction, reformation of the trans conjugate base from this intermediate, is ~60 kJ/mol. This energy is much higher than that for the cis isomer, which is ~9−15 kJ/mol. *This implies that nucleophiles can attack the trigonal bipyramid solely cis to* NH_2^-*; the attack trans to* NH_2^- *is not competitive since its activation energy is higher by ~50 kJ/mol.*

In the transition state *trans*-Co$(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$, the Co···Cl bond is completely broken and the CoN_5 chromophore is trigonal bipyramidal in contrast to the corresponding cis isomer (Figures 2a and S3, Supporting Information). The imaginary mode describes the rearrangement of the square pyramid into the trigonal bipyramid. A component describing the elongation of the Co···Cl bond is absent because this process is already completed. The p_π lone pair of NH_2^- still forms the already described π and π^* MOs (as in Figure 1a and 1b).

Substitution Pathway via the Hexacoordinated Intermediate *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^+$. Geometry optimization of the cis conjugate base in its first excited triplet state leads to a stable species exhibiting a triplet ground state, *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^+$ (Table 1, Figure S4, Supporting Information). Within the error limits of the present computations ($\lesssim$10−15 kJ/mol) its energy is equal to those of the trigonal bipyramidal pentacoordinated intermediates *cis*- and *trans-eq-tbp*-Co$(NH_3)_4(NH_2)\cdot Cl^+$ (Tables 1 and S1, Supporting Information, Scheme 1). In previous studies,[5,9] the *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^+$ species, exhibiting a triplet ground state, has been denoted as "hexacoordinated intermediate", and this appellation is kept. In comparison with the conjugate base (Figure S2, Supporting Information), the Co−N(H_2) bond (Figure S4, Supporting Information) is shorter by ~0.13 Å due to occupation of the $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$ MO by a single electron (Figure 3a). The bonds lying in the axis of the $d_\sigma^*(Co-Cl)$ MO (Figure 3b) are elongated strikingly because of its population by one electron. The energy of *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^+$ is considerably lower than that of any trans intermediate with a triplet or quintet ground state (see below), and furthermore, it is not much higher than that of the conjugate base (Table 1, Scheme 1). This intermediate, exhibiting a low energy and a weak Co···Cl bond, could also account for the high reactivity of the conjugate base *cis*-Co$(NH_3)_4(NH_2)Cl^+$.

The reactant $Co(NH_3)_5Cl^{2+}$ and the conjugate bases *cis*- and *trans*-Co$(NH_3)_4(NH_2)Cl^+$ exhibit a low-spin d^6 electron configuration as for virtually all of the amine complexes of Co^{III}. The ground state of the hexacoordinated intermediate *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^+$, however, is a triplet. Because of the spin change occurring during the transformation of the conjugate base into this intermediate, the geometry of the transition state *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ was computed as a MECP. At this geometry, the energies of the singlet and triplet states are equal and minimal. Its geometry (Figure 4) is roughly intermediate between that of the conjugate base *cis*-Co$(NH_3)_4(NH_2)Cl^+$ (Figure S2, Supporting Information) and the hexacoordinated intermediate (Figure S4, Supporting Information). The MECP energies of the singlet and triplet states, computed at the MCQDPT2 level, differ by only 4.1 kJ/mol, which is well within the error limits of the computational method. More significantly, OPBE and MCQDPT2 activation energies ($\Delta E^\ddagger$) agree within ~2 kJ/mol (Table 1). This corroborates the accuracy of the OPBE geometry. If the latter was poor, the MCQDPT2 energies for the singlet and triplet and/or the OPBE and the MCQDPT2 energies would differ considerably (by $\gtrsim$15 kJ/mol).

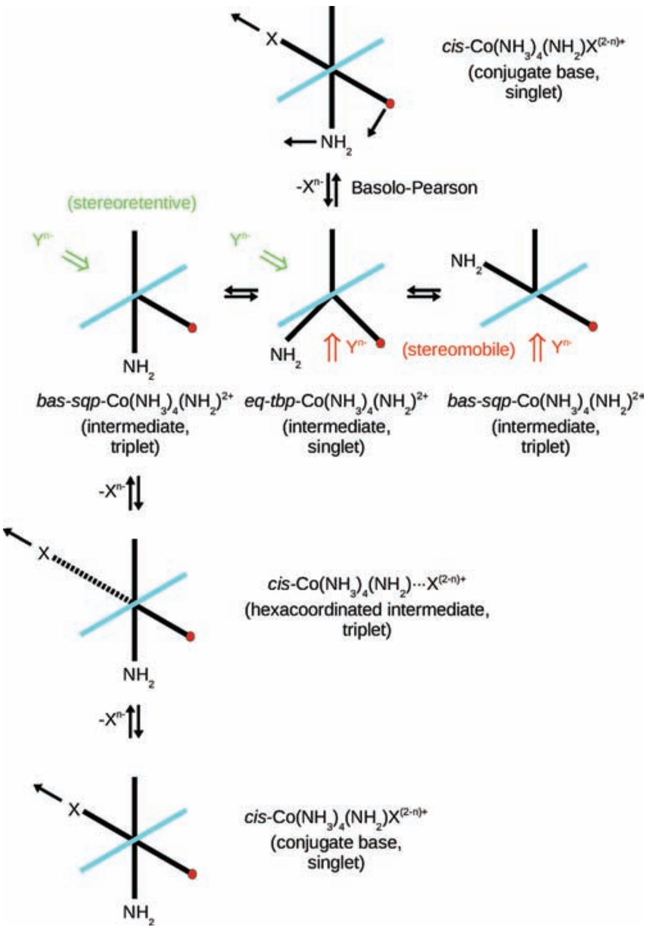
The transition state for substitution of the hexacoordinated intermediate via the D mechanism *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ with an electronic triplet state exhibits a long Co···Cl bond, and the imaginary mode represents the severance of the Co···Cl bond (Figure S5, Supporting Information). The activation energy of ~6 kJ/mol is somewhat lower than that for the back reaction via the MECP (Tables 1 and S1, Supporting Information, Scheme 1). The corresponding square pyramidal pentacoordinated intermediate *cis-bas-sqp*-Co$(NH_3)_4(NH_2)\cdot Cl^+$ (*bas* means that NH_2^- is located in the basal plane) has a triplet ground state and exhibits an insignificantly higher energy (of 4−5 kJ/mol) than the hexacoordinated intermediate (Tables 1 and S1, Supporting Information, Scheme 1). The leaving Cl^- ligand is located in the second coordination sphere at 4.05 Å of the Co center.

Rearrangement of Pentacoordinated Intermediates Co$(NH_3)_4(NH_2)^{2+}$. Chloride elimination from the conjugate bases *cis*- and *trans*-Co$(NH_3)_4(NH_2)Cl^+$, leading to the trigonal bipyramidal intermediates *cis*- and *trans-eq-tbp*-Co$(NH_3)_4(NH_2)\cdot Cl^+$, takes place without spin change. The leaving ligand Cl^- is located in the second coordination sphere, either cis (Figure 2b) or trans to NH_2^-. These two isomers, in which the NH_2^- ligand is planar, exhibit virtually equal energies (Table S1, Supporting Information). Chloride elimination from the hexacoordinated intermediate *cis*-Co$(NH_3)_4(NH_2)\cdots Cl^+$, exhibiting a triplet ground state, leads to the square pyramidal intermediate *cis-bas-sqp*-Co$(NH_3)_4(NH_2)\cdot Cl^+$ with Cl^- in the second coordination sphere. The NH_2^- ligand, located in the basal plane, is pyramidal in all of these species with a triplet ground state (Figures 4, S4, and S5, Supporting Information; Scheme 5).

For computation of the rearrangement of the above-mentioned trigonal bipyramidal and square pyramidal pentacoordinated intermediates, the Cl^- ion in the second coordination sphere was dropped. The trigonal bipyramidal intermediate *eq-tbp*-Co$(NH_3)_4(NH_2)^{2+}$ (Figure 5) exhibits a planar NH_2^- group and the $NH_3-Co-NH_3$ angle in the trigonal plane is 87.3°. It should be noted that MO 29 (the HOMO is MO 32) is the $p_\pi(NH_2^-)$ lone pair stabilized by the formally empty $d_{x^2-y^2}$ orbital of Co^{III} exactly as proposed more than 50 years ago by Basolo and Pearson.[17] The present computations substantiate their hypothesis. Since rearrangement of this species into *bas-sqp*-Co$(NH_3)_4(NH_2)^{2+}$, exhibiting possibly a slightly higher energy (Table 1), involves a spin multiplicity change (from 1 to 3), the transition state connecting these two intermediates had to be computed as a MECP. The activation energy for this process is ~8−10 kJ/mol (Table 1), and hence, its rate constant is ~10^{11} s^{-1}.

Rearrangement of *eq-tbp*-Co$(NH_3)_4(NH_2)^{2+}$ via Berry pseudorotation does not take place, since this process requires a high activation energy (Table 1, Schemes 2 and 3): it would involve two steps, the first being opening of the $NH_3-Co-NH_3$ angle (87.3°) in the trigonal plane of *eq-tbp*-Co$(NH_3)_4(NH_2)^{2+}$ to yield the transition state $Co(NH_3)_4(NH_2)^{2+\ddagger}$ with an angle of 139.8° (Figure S6, Supporting Information). This process

Scheme 5



requires an activation energy of 54−56 kJ/mol, and therefore, it is not at all competitive with the already mentioned reactions of *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ (Tables 1 and S1, Supporting Information). The subsequently formed intermediate *ap-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ with an $NH_3-Co-NH_3$ angle of 174.2° also has a high energy (Tables 1 and S1, Supporting Information) with respect to *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ and *bas-sqp*-$Co(NH_3)_4(NH_2)^{2+}$. Switching of the $NH_3-Co-NH_3$ axis takes place via a 90° rotation (Figure S7, Supporting Information) of the apical NH_2^- ligand, which is virtually activationless (Table 1, Scheme 3). Finally, the other isomer of *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ is formed via reduction of the $NH_3-Co-NH_3$ angle of the two other basal ammonia ligands.

The two axial NH_3 ligands keep their position in the *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ to *bas-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ rearrangement, NH_2^- remains in the basal or trigonal plane, and nucleophile (Y^{m-}) entry leads *exclusively* to *cis*-$Co(NH_3)_4(NH_2)Y^{(2-m)+}$ (Scheme 5); no *trans*-$Co(NH_3)_4(NH_2)Y^{(2-m)+}$ is formed.

Chloride Substitution by Azide and Water via a Stereomobile I_d Mechanism. In the presence of N_3^-, more than 50% *cis*-$Co(NH_3)_4(^{15}NH_3)N_3^{2+}$ is formed and for some leaving ligands like DMSO H_2O entry leads to slightly more than 50% *cis*-$Co(NH_3)_4(^{15}NH_3)OH^{2+}$.[20] This means that a stereomobile pathway must exist, which has to be competitive with the Basolo−Pearson mechanism or the pathway via the hexacoordinated intermediate, since the latter two mechanisms cannot yield more than 50% *cis*-$Co(NH_3)_4(^{15}NH_3)N_3^{2+}$ or *cis*-$Co(NH_3)_4(^{15}NH_3)OH^{2+}$ (Scheme 5).

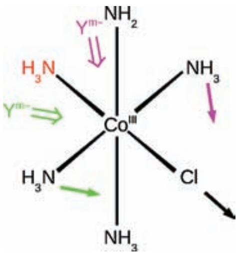


Figure 6. Sites of nucleophile entry in the stereomobile I_d pathway (Y^{m-}, for example N_3^-, OH_2).

In such a stereomobile pathway, the nucleophile, for example N_3^-, must enter adjacent to $^{15}NH_3$ and elimination of Cl^- must occur concerted with rearrangement of at least one NH_3 ligand (Figure 6). The reactant *cis*-$Co(NH_3)_4(NH_2)Cl\cdot N_3$ (Figure S8, Supporting Information), exhibiting a singlet electronic state, corresponds to this starting point. Among numerous attempts to compute the corresponding transition state, only calculation for a single structure was successful; it yielded the pseudotrigonal bipyramidal *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^{\ddagger}$ species (Figure 7a) with a triplet electronic state and NH_2^- in the axial position. The distances between the three anions, NH_2^-, Cl^-, and N_3^-, are maximal (Figure 7a). The imaginary mode describes the rearrangement of the NH_3 ligands in the trigonal plane, elongation of the $Co\cdots Cl$ bond, and shortening of the $Co\cdots N_3$ bond. Because of the long bonds of the exchanging ligands in the transition state, this stereomobile pathway is classified as I_d.[49] The product, *cis*-$Co(NH_3)_4(NH_2)N_3\cdot Cl$ (Figure S9, Supporting Information), has a singlet electronic state. The activation energy for this I_d pathway is only slightly and insignificantly higher (by 5 kJ/mol) than that for the Basolo−Pearson mechanism (Table 1, Scheme 1).

This pathway is quite uncommon because reactant and product exhibit a singlet electronic state, whereas the transition state has a triplet state. In this case, the first spin change takes place during elongation of the Co−Cl bond, which is concerted with rearrangement of NH_3 ligands (Scheme 6). Likewise, the second spin change takes place during formation of the $Co-N_3$ bond, which is also concerted with rearrangement of NH_3 ligands.

The structure and imaginary mode of the corresponding transition state *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH_2)^{+\ddagger}$ (triplet state) for the stereomobile substitution by water resemble those of the corresponding azide species and so does also the activation energy (Table 1).

The analogous transition state for the reaction with hydroxide, *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH)^{\ddagger}$, exhibits a similar structure but a different imaginary mode (Figure 7b), which represents elimination of Cl^- concerted with formation of a square pyramidal pentacoordinated intermediate (the Co center does not move toward OH^- to form the Co−O(H) bond).[50,51] Hence, this is a transition state for a stereomobile D pathway. In a second step, water, for example, could add to this species to form the product (Figure 7b). Consistent with Green and Taube's finding,[14,15] OH^- is not the entering ligand, probably because OH^- in the second coordination sphere forms strong H bonds with 3 facial NH_3 ligands. Breaking of a strong H bond requires a sizable energy, whereas water, forming weaker H bonds, is more readily available for Co−O formation.

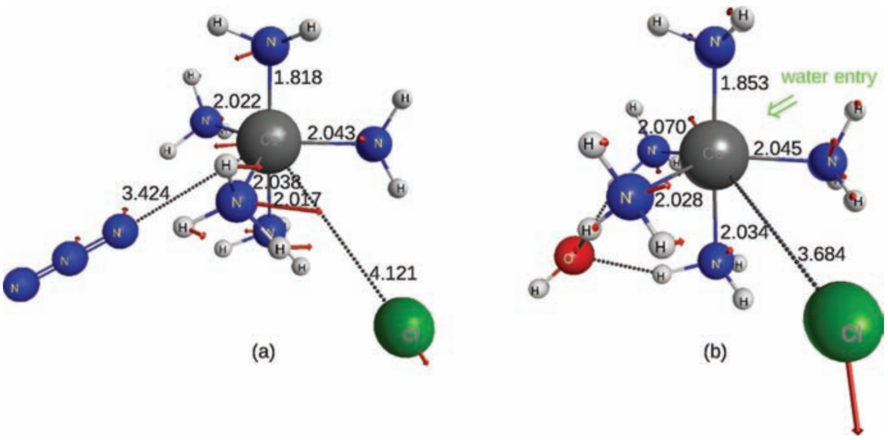
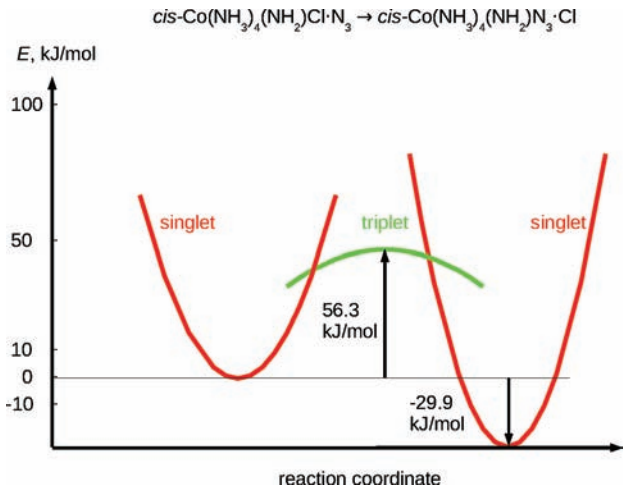


Figure 7. Perspective view, cobalt(III)−ligand bond lengths (Å), and imaginary modes (52*i* and 19*i* cm^{-1}, respectively) of the transition states *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^{\ddagger}$ (a) and *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH)^{\ddagger}$ (b) for stereomobile Cl^- substitution via the I_d and D mechanisms (triplet state).

Scheme 6



Intermediate *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl^+$. To verify, whether a labile low-spin Co^{II} center could account for the high reactivity of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$, the intermediate *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl^+$, formed via transfer of a $\pi(d_\pi(Co)-p_\pi(NH_2^-))$ electron into the $d_\sigma^*(Co-Cl)$ MO, which is essentially a $p_\pi(NH_2^-)$ to Co^{III} charge transfer, was also investigated. The corresponding vertical singlet−triplet energy is very high (Table 2), and it remains so after optimization of its geometry (Table 1). Since this energy is much higher than the free activation enthalpy for aquation of $Co(NH_3)_5Cl^{2+}$ (106 kJ/mol[10,11,13,48]), formation of a labile Co^{II} center can be excluded; this pathway does not operate. The oxidized $NH_2^{\bullet}$ ligand is a weaker donor than NH_2^-. As a consequence, the $Co^{II}-N^{\bullet}(H_2)$ bond is longer (Figure S10, Supporting Information). As in the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$, the bonds lying in the axis of the $d_\sigma^*(Co-Cl)$ MO are elongated, whereby the Co···Cl bond is shorter (by ∼0.15 Å).

Intermediate *cis*-$Co(NH_3)_4(NH_2)Cl^+$ in the Quintet State. In this intermediate, the NH_2^- ligand is planar (Figure S11, Supporting Information) as in the corresponding trans isomer (see below). The vertical singlet−quintet transition energy is high and similar to that of the trans isomer (Table 2). Its energy at the relaxed geometry is higher than those of the trigonal bipyramidal pentacoordinated intermediates *cis*- and *trans-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ and the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (Tables 1 and S1, Supporting Information).

***trans*-$Co(NH_3)_4(NH_2)Cl^+$ Intermediates with Triplet and Quintet States.** Their geometries (Figures S12 and S13, Supporting Information) were computed starting from the lowest vertical triplet and quintet states of the conjugate base (Table 2). All attempts to compute the geometry of the higher triplet state, in which the $d_\sigma^*(Co-Cl)$ MO is populated, failed. In both intermediates, the Co−Cl bond is elongated slightly (Figures S12 and S13, Supporting Information) but two or four $Co-N(H_3)$ bonds, respectively, are elongated considerably in the triplet and quintet species. Because of their relatively high energies (Tables 1 and S1, Supporting Information), both intermediates are unlikely to give rise to a facile Cl^- substitution in spite of the trans effect.[52]

pK_a of the Intermediates *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ and *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$. To elucidate the stage of back-protonation, the pK_a values of the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ and the trigonal bipyramidal pentacoordinated intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ were calculated. In the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$, the $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$ MO is populated by a single electron in contrast to its corresponding conjugate base, in which its occupation is two. Thus, it is obvious that the hexacoordinated intermediate is less basic than its corresponding conjugate base. On the basis of the energy of the intermediate $Co(NH_3)_5Cl^{2+}$ in its triplet state (91.6 kJ/mol, obtained from the total energies in Table S1, Supporting Information) with respect to that of the reactant $Co(NH_3)_5Cl^{2+}$ (exhibiting a singlet ground state), and in comparison with the energy of the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (24.4 kJ/mol, Table 1) with respect to the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$, the pK_a difference between the conjugate acid of *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ ($Co(NH_3)_5Cl^{2+}$ with a triplet state) and $Co(NH_3)_5Cl^{2+}$ (singlet state) can be calculated as 11.8: $\Delta pK_a = (\log e)(91.6-24.4)/(RT)$. Assuming that the p$K_a$ of the equally charged $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5NO_2^{2+}$ ions, the latter being 16.8,[53] are similar, the pK_a of the hexacoordinated intermediate is estimated as ∼5, and this species will certainly not be protonated in alkaline medium. In an analogous way, the pK_a of the conjugate acid

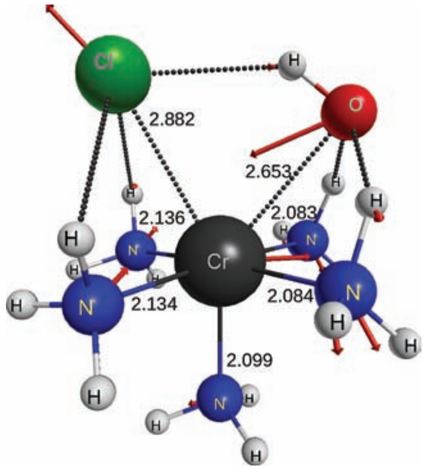


Figure 8. Perspective view, chromium(III)−ligand bond lengths (Å), and imaginary mode (192*i* cm^{-1}) of the transition state $Cr(NH_3)_5 \cdots Cl(OH)^{+\ddagger}$ for Cl^- substitution by OH^- via the I_a mechanism (quartet state).

of *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ ($Co(NH_3)_5^{3+}$ with an electronic singlet state) is estimated as ∼−6. This very low pK_a is due to the strong stabilization of the p_π lone pair of NH_2^- as postulated by Basolo and Pearson.[17] Hence, it can be excluded that the pentacoordinated intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ will be protonated.

Transmission Coefficient (κ) and Rate Constant for Transformation of the Conjugate Base *cis*-Co(NH$_3$)$_4$(NH$_2$)Cl$^+$ into the Hexacoordinated Intermediate *cis*-Co(NH$_3$)$_4$(NH$_2$)···Cl$^+$. For reactions involving spin changes, the transmission coefficient κ might be smaller than 1; therefore, its value was computed based on the Eyring equation[54,55] and semiclassical theory for estimation of electron transfer rates.[56,57] The detailed procedure is described in the Supporting Information. For transformation of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ into the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$., κ was estimated as ∼0.06.

Base Hydrolysis of Chloro Pentaammine Complexes of Cr^{III}, Ru^{III}, and Rh^{III} via the Basolo−Pearson Mechanism. There are no remarkable structural differences between the conjugate bases *cis*-$M(NH_3)_4(NH_2)Cl^+$ and the trigonal bipyramidal pentacoordinated intermediates *cis-eq-tbp*-$M(NH_3)_4(NH_2)\cdot Cl^+$ (M = Cr, Ru, and Rh) compared with the corresponding species of cobalt(III). Since, in contrast to ruthenium(III) and rhodium(III), the trigonal bipyramidal pentacoordinated intermediate *cis-eq-tbp*-$Cr(NH_3)_4(NH_2)\cdot Cl^+$ has a low energy (Tables 1 and S1, Supporting Information), the corresponding transition state *cis*-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ was computed as well; its imaginary mode (Figure S14, Supporting Information) is the same as that of cobalt(III) (Figure 2a). The activation energy for this reaction is even slightly lower than that of cobalt(III) (Table 1).

Chloride Substitution in Chloro Pentaammine Chromium(III) by Hydroxide via the I$_a$ Mechanism. This pathway, proceeding with retention of configuration,[49,58] was investigated to discuss the favored mechanism of the base-catalyzed chloride substitution. The transition state $Cr(NH_3)_5\cdots Cl(OH)^{+\ddagger}$ (Figure 8) resembles that for the aquation,[48] and within the estimated error limits of ≲10−15 kJ/mol, the computed activation energy of 99.6 kJ/mol (Table 1) agrees with experiment (k_{OH}(25.3 °C) = 0.00192 M^{-1} s^{-1}, $\Delta G^\ddagger$ = 88.5 kJ/mol).[59]

■ DISCUSSION

Mechanism of the Base Hydrolysis Reaction. Three substitution mechanisms with low activation energies are available (Table 1, Scheme 1). They all involve deprotonation of an ammonia ligand cis to the leaving ligand. The first mechanism, proceeding via the trigonal bipyramidal intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ (Figure 5) exhibiting a singlet ground state, was postulated by Basolo and Pearson[17] in 1956. The second mechanism involves the hexacoordinated intermediate[4,5] *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ with a triplet ground state.[9] The third mechanism had to be searched for in order to account for the stereochemistry of this reaction. This pathway does not proceed via any intermediate.

Although the conjugate base with the deprotonated ammonia ligand trans to the leaving ligand is thermodynamically slightly more stable and expected to have an enhanced reactivity due to the trans effect,[52] such pathways are by no means competitive, regardless of whether they would proceed via singlet or triplet PESs. Furthermore, for both sites of deprotonation, reactions via quintet states do not take place. The mechanism via a low-spin *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})Cl^+$ species[19] can be ruled out because of its very high activation energy.

Lifetime (τ_I) of the Intermediates. τ_I was estimated as described in previous work.[60] The hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ can transform very rapidly (within ∼2 ps) into the square pyramidal pentacoordinated intermediate *cis-bas-sqp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$. Chloride substitution in *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ by water or azide, for example, is expected to take place at a similar rate. τ_I of the hexacoordinated intermediate is thus on the order of ∼2 ps. With respect to formation of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$; however, τ_I would be longer, ∼40−50 ps.

The trigonal bipyramidal intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ equilibrates with square pyramidal *bas-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ within ≲10 ps, whereas with respect to formation of the conjugate base, its lifetime might be longer (∼5.2−71 ps). The interconversion (Scheme 5) of hexacoordinated, square pyramidal, and trigonal bipyramidal intermediates is very fast and occurs on the time scale of ≲10 ps. With respect to formation of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$, the lifetime of the intermediates is longer but less than ∼100 ps.

Origin of the High Reactivity of the Hexacoordinated Intermediate *cis*-Co(NH$_3$)$_4$(NH$_2$)···Cl$^+$. In cis and trans isomers of deprotonated amine complexes of cobalt(III), the (occupied) antibonding $\pi^*(d_\pi(Co)-p_\pi(NH_2^-))$ level (Scheme 4, Figures 1b and 3a), exhibiting a higher energy than the d_π levels of cobalt(III), is responsible for a reduction of the crystal field splitting parameter Δ. This is manifested in low vertical singlet−triplet excitation energies in the conjugated bases (Table 2). The excitation energy is lower for the cis isomer because in the latter the lowest unoccupied MO (LUMO) is located in the $(H_3)N-Co-Cl$ axis (Figure 3b) whereas in the trans isomer the LUMO, with a ∼$d_{x^2-y^2}$ shape (Figure 1d), lies in the $Co(NH_3)_4$ plane. Its higher energy (Scheme 4) is due to NH_3 being a stronger σ donor than Cl^-. Hence, for weak leaving ligands (X^{n-}), the triplet energy of cis isomers is lower than for the trans ones.

For the trans isomer, a reactive intermediate exhibiting a relatively low energy does not exist. In the *trans*-$Co(NH_3)_4(NH_2)Cl^+$ intermediate in its lowest triplet state, two $Co-N(H_3)$ bonds are elongated (Figure S12, Supporting Information). In this intermediate, ammonia substitution, but not chloride substitution, would be accelerated. Labilization of the Cl^- ligand would require population of d_σ^*(Co−Cl) MO, which is not the LUMO (Scheme 4). Its energy is high (Table 2) because the NH_2^- ligand, which is a strong p_π and a strong σ donor as well, is located in the Co−Cl axis. Hence, for trans isomers, a substitution-labile low-lying hexacoordinated intermediate cannot exist. Of course, due to the trans effect, the conjugate base *trans*-$Co(NH_3)_4(NH_2)Cl^+$ is more reactive than $Co(NH_3)_5Cl^{2+}$, but for the reasons discussed above, it is less reactive than the cis isomer.

Stereochemistry. Base hydrolysis of *trans*-$Co(NH_3)_4(^{15}NH_3)X^{(3-n)+}$ via Basolo and Pearson's[17] trigonal bipyramidal pentacoordinated intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ would lead to exactly 50% *cis*-$Co(NH_3)_4(^{15}NH_3)Y^{(3-m)+}$ and 50% *trans*-$Co(NH_3)_4(^{15}NH_3)Y^{(3-m)+}$ for any nucleophile Y^{m-} (Scheme 5) because nucleophile entry trans to NH_2^- is unfavorable (Table 1, Scheme 1). This ratio is independent of the equilibration of the trigonal bipyramidal intermediate with the square pyramidal one. A rearrangement of the pentacoordinated intermediates via Berry pseudorotation does not take place due to its high activation energy (Table 1, Schemes 2 and 3). The same stereochemistry is expected for reaction via the hexacoordinated intermediate, provided that the latter does not undergo ligand substitution via the I_d mechanism and that nucleophile addition at the subsequently formed square pyramidal pentacoordinated intermediate (with a triplet ground state) does not compete with rearrangement into the trigonal bipyramid. The reaction would be stereoretentive in the case in which the entering ligand would displace the weakly bound leaving ligand (in the hexacoordinated intermediate) via the I_d mechanism in an "adjacent attack"[40,49,58,61] or if nucleophile addition to the square pyramidal pentacoordinated intermediate is much faster than rearrangement into the trigonal bipyramidal intermediate (with a singlet ground state). The accuracy of the present computations ($\lesssim$10−15 kJ/mol) is insufficient for an accurate determination of the product ratios arising from these processes. In the fully stereomobile pathway (Scheme 6, Figures 6, 7, S8, and S9, Supporting Information), *trans*-$Co(NH_3)_4(^{15}NH_3)X^{(3-n)+}$ is converted into (100%) *cis*-$Co(NH_3)_4(^{15}NH_3)Y^{(3-m)+}$ (Y^{m-}: for example, N_3^- or OH_2).

In the base hydrolysis of *trans*-$Co(NH_3)_4(^{15}NH_3)Cl^{2+}$ in NaOH 0.05 and 1.0 M, respectively, 46% and 43% *cis*-$Co(NH_3)_4(^{15}NH_3)OH^{2+}$ are formed at 25 °C.[20] Reaction in 0.05 M NaOH/1.0 M NaN_3 (25 °C) produces $Co(NH_3)_4(^{15}NH_3)OH^{2+}$ (91.3%) and $Co(NH_3)_4(^{15}NH_3)N_3^{2+}$ (8.7%), whereby 43% of the $Co(NH_3)_4(^{15}NH_3)OH^{2+}$ product has the cis configuration.[20] For $Co(NH_3)_4(^{15}NH_3)N_3^{2+}$ formation, the stereomobile pathway contributes to at least 40%, since 70% of the product is in the cis configuration. Base hydrolysis of $Co(NH_3)_5OS(CH_3)_2^{3+}$, exhibiting the neutral leaving ligand dimethyl sulfoxide, in the presence of NaN_3 is less stereomobile, since it yields ~60% *cis*-$Co(NH_3)_4(^{15}NH_3)N_3^{2+}$, but a minor part of H_2O addition has to proceed via the stereomobile pathway (~51−54% of *cis*-$Co(NH_3)_4(^{15}NH_3)OH^{2+}$ is formed).[20] This experimental data shows clearly that a fully stereomobile pathway exists.

For water as a nucleophile ($Co(NH_3)_5OH_2^{3+}$ is formed via H_2O, not OH^- entry[14,15]), less than 50% cis product was obtained for Cl^-, Br^-, and NO_3^- as leaving ligands.[20] This means that this product might be formed mainly via the Basolo−Pearson mechanism or the hexacoordinated intermediate, which subsequently forms the pentacoordinated intermediates at equilibrium (Scheme 5). The small amount (~10%) of stereoretention arises from direct substitution at the hexacoordinated intermediate via the I_d mechanism or nucleophile addition at the square pyramidal pentacoordinated intermediate being not much slower than rearrangement into the trigonal bipyramidal intermediate (see above). Retention (<50% cis product) can only be rationalized by the pathway involving the hexacoordinated intermediate. Stereomobility (>50% cis product) must arise from the concerted stereomobile mechanism.

The stereochemical results[20] do not allow to assess, whether the Basolo−Pearson intermediate is formed via the Basolo−Pearson transition state (Figure 2a) or via the hexacoordinated intermediate and its corresponding MECP (Figures 4 and S4, Supporting Information). The present calculations do not allow exclusion of an approximate 1:1 *cis/trans*-$Co(NH_3)_4(^{15}NH_3)Y^{(3-m)+}$ product ratio arising from the stereoretentive mechanism via the hexacoordinated intermediate and the fully stereomobile pathway (which would be approximately equally fast). The computed higher activation energy for the Basolo−Pearson mechanism cannot be taken as evidence against that hypothesis because this energy difference lies within the error limits.

Base Hydrolysis of Cobalt(III) Complexes with Chelating or Bulky Amine Ligands. A variety of cobalt(III) complexes with chelating or bulky amine ligands have been synthesized to determine stereochemical reactant−product relationships.[1−3] On their basis, evidence for the presence or absence of pentacoordinated intermediates and their structures were derived. *In most cases, it was assumed that a single mechanism accounts for this reaction*, and as a consequence, the experimental results were interpreted on the basis of the presence or absence of a *single intermediate* with either a trigonal bipyramidal or a square pyramidal structure. The present study shows unequivocall, that three mechanisms exist, which involve either no intermediate, but a transition state with triplet state (Scheme 6), or an intermediate with a trigonal bipyramidal, square pyramidal, or hexacoordinated structure (Scheme 5). Bulky or chelating ligands obviously favor or disfavor certain intermediates or transition states, and the preferred mechanism will depend on the ligands.

A discussion of the vast amount of literature on the base hydrolysis reaction of cobalt(III) complexes with such amine ligands is beyond the scope of the present article. The present study supplies the means for assessment of the mechanism: the energy difference between the trigonal bipyramidal pentacoordinated intermediate in its (closed shell) singlet ground state and the corresponding square pyramidal intermediate with a triplet ground state gives a first clue about the preferred mechanism. In many cases, this difference will be sizable; hence, either the singlet or the triplet could then be excluded. In a second step, further details can be obtained by computation of intermediates, transition states, and MECPs for the three mechanisms.

Base Hydrolysis of Analogous Complexes of Chromium(III), Ruthenium(III), and Rhodium(III). The pathway via the hexacoordinated intermediate is unfavorable for amine complexes of chromium(III), ruthenium(III), and rhodium(III).[9] For ruthenium(III) and rhodium(III), the Basolo−Pearson mechanism[17] is unlikely to operate, since the trigonal bipyramidal pentacoordinated intermediates *cis-eq-tbp*-$Ru(NH_3)_4(NH_2)\cdot Cl^+$ and *cis-eq-tbp*-$Rh(NH_3)_4(NH_2)\cdot Cl^+$ exhibit much higher energies (>70 kJ/mol, Table 1) than the conjugate bases *cis*-$M(NH_3)_4(NH_2)Cl^+$ (M = Ru, Rh). Furthermore, these energies are much higher than for the corresponding reaction of cobalt(III). For chromium(III), however, activation energy and energy of the trigonal bipyramidal pentacoordinated intermediate are comparable to cobalt(III) (Table 1). For $Cr(NH_3)_5Cl^{2+}$, the experimental second-order rate constant for base hydrolysis is smaller by a factor of >100 than for $Co(NH_3)_5Cl^{2+}$.[12,59] The lower reactivity of chromium(III) might arise from a higher pK_a of the *cis*-NH_3 ligands which could be due to the longer Cr−N(H_3) bond lengths (by ~0.17 Å) compared with Co−N(H$_3$). It should be noted that the computed activation energy (Table 1) for chloride substitution by hydroxide via the I$_a$ mechanism agrees with experiment (Results). Since the pK_a of the *cis*-NH$_3$ ligands of Cr(NH$_3$)$_5$Cl^{2+} is unknown, the substitution mechanism cannot be attributed on the basis of the pertinent data in Table 1. The Basolo−Pearson mechanism[17] would be competitive to the I$_a$ pathway, provided that pK_a(*cis*-NH$_3$) is <21.9 (for Co(NH$_3$)$_5$Cl^{2+}, pK_a(*cis*-NH$_3$) ≈ 18−19). Substitution via the I$_a$ pathway would proceed with retention of the configuration, whereas the Basolo−Pearson mechanism[17] would give rise to 50% stereomobility.

The relatively low energy and high reactivity of the hexacoordinated intermediate *cis*-Co(NH$_3$)$_4$(NH$_2$)···Cl$^+$ are due to a low energy for the transition of a $\pi^*(d_\pi(\mathrm{Co})-p_\pi(\mathrm{NH_2}^-))$ electron into the d_σ^*(Co−Cl) level (Scheme 4, Figure 3). For the valence isoelectronic rhodium(III) and iridium(III) complexes, the crystal field splitting parameter Δ is larger and, therefore, the energy of the corresponding hexacoordinated intermediates would be higher.[9] For these metal centers, the pathway via the triplet state is not the most favorable. For ruthenium(III), Δ is also large but, furthermore, the $\pi^*(d_\pi(\mathrm{Ru})-p_\pi(\mathrm{NH_2}^-))$ MO is populated by a single electron. Its promotion into the d_σ^*(Ru−Cl) level would lead to a rather high-lying excited state (because of the absence of the stabilizing spin-pairing energy).[9] For ruthenium(III), the associative pathway is anyway advantageous for electronic reasons.[40,49,58] For chromium(III), Δ is similar to cobalt(III) but, as for ruthenium(III), the $\pi^*(d_\pi(\mathrm{Cr})-p_\pi(\mathrm{NH_2}^-))$ MO is populated by a single electron. The excited state arising from population of the d_σ^*(Cr−Cl) level does not have a low energy.[9]

The pathway, involving a low-lying triplet state, is unique for low-spin d^6 systems with a small Δ, and it is feasible solely for amine complexes of cobalt(III).[9]

SUMMARY

Three pathways are feasible for the base hydrolysis of ammine complexes of cobalt(III), which all proceed via deprotonation of an amine ligand cis to the leaving group: (i) the mechanism proposed by Basolo and Pearson[17] involving a trigonal bipyramidal pentacoordinated intermediate with a singlet ground state, (ii) the mechanism proceeding via a hexacoordinated intermediate with a triplet ground state,[4,5,9] and (iii) the stereomobile I$_d$ pathway via a transition state exhibiting a triplet ground state.

In the absence of strain or constraints in the ligand sphere, the Basolo−Pearson mechanism yields 50% retention and 50% stereomobility (nucleophile entry trans to the deprotonated amine and the Berry pseudorotation are unfavorable).

The mechanism via the hexacoordinated intermediate can proceed with full retention of configuration (if substitution at the intermediate takes place via the I$_d$ mechanism or if nucleophile addition at the subsequently formed square pyramidal pentacoordinated intermediate is much faster than rearrangement into the trigonal bipyramidal intermediate) or it can yield the same stereochemistry as the Basolo−Pearson mechanism (provided that rearrangement into the trigonal bipyramid is much faster than the rates of the stereoretentive reactions). Depending on the rate constants of these processes, reactions via the hexacoordinated intermediate or the corresponding square pyramidal pentacoordinated intermediate can proceed with 0−50% stereomobility and 100−50% stereoretention.

The pathway via the I$_d$ transition state with a triplet state is fully stereomobile.

For the pentaammine complexes of cobalt(III), exhibiting minimal strain in the ligand sphere, all three of these pathways might operate, whereas in systems with chelating ligands, where strain or constraints are present, certain mechanisms might be favored and others disfavored.

Protonation of the penta- or hexacoordinated intermediates does not take place; protonation occurs after nucleophile entry or for water eventually concerted with its entry. (Due to the high pK_a of the products, protonation of their conjugate bases takes place at a diffusion-controlled rate).

These three mechanisms do not operate for the corresponding complexes of ruthenium(III), rhodium(III), and iridium(III).

The Basolo−Pearson mechanism might operate for amine complexes of chromium(III).

This study demonstrates that the present quantum chemistry codes, in particular GAMESS,[21,22] are capable to treat complex reaction systems in solution.

ASSOCIATED CONTENT

Supporting Information. Procedure for calculation of κ; total energies of all of investigated species; experimental and computed cobalt(III)−ligand bond lengths in the Co(NH$_3$)$_5$Cl^{2+} ion; atomic coordinates; computed k_+ and k_- values; perspective view of other computed species, reactants, transition states, intermediates, and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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