120. Base Hydrolysis of (Acidato)(Pentaamine) Complexes with Inert Metal Centers: Electronic Structure of the Intermediates, Requirements for Their Formation, and the Unique Reactivity of the Complexes of Cobalt(III)

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Molecular-orbital calculations have been performed for the conjugate bases *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ and *trans*-$[M(NH_3)_4(NH_2)Cl]^+$ ($M = Cr^{III}$, Co^{III}, and Rh^{III}), the hexacoordinated intermediates *cis*- and *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$, the square-pyramidal and trigonal bipyramidal pentacoordinated intermediates *apical*-$[Co(NH_3)_4(NH_2)]^{2+}$, *basal*-$[Co(NH_3)_4(NH_2)]^{2+}$, and *equatorial*-$[M(NH_3)_4(NH_2)]^{2+}$ (M = Co and Rh), respectively, using modified extended *Hückel* and SCF MS-Xα methods. The LUMO of the conjugate bases is an antibonding metal centered d_{σ^*} orbital which is stabilized during the dissociative activation of the M–Cl bond. For the above conjugate bases, separations of the highest doubly occupied MO (HDOMO) and the LUMO of 1.3, 2.5, 1.8, and 2.5 eV, respectively, have been calculated using the SCF MS-Xα model. Only in the conjugate base *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ with the smallest HDOMO – LUMO gap, the singlet electronic structure of the ground state may be stabilized by changing into a triplet when the Co–Cl bond is activated. This situation is unique to (acidato)(pentaamine)cobalt(III) complexes with the deprotonated amine ligand *cis* to the leaving group and the reason for the existence of intermediates and their reactivity as well. Base hydrolysis of the analogues Cr^{III} and Rh^{III} complexes – the latter taken to represent the second- and third-row transition-metal amines – is unlikely to proceed *via* intermediates; a concerted substitution process is expected to take place.

Introduction. – In general, thermally activated substitution reactions involving octahedral transition-metal complexes are believed to be concerted, *i.e.* they do not proceed *via* intermediates. In this study, we raise the hypothesis that – at least for the alkaline hydrolysis [1] of (acidato)(pentaamine) complexes – intermediate formation is only possible, if a stabilization of the electronic structure occurs along with the dissociative activation for the substitution process.

The base hydrolysis of (acidato)(pentaamine)cobalt(III) complexes (*Scheme, a*) was believed [1] to proceed *via* pentacoordinated intermediates (*Scheme, a*) whose existence has been established [2] [3] only very recently. The most frequently studied $[Co(NH_3)_5X]^{n+}$ complexes (*Scheme, b*) do not form long-lived[1]) pentacoordinated intermediates. The latter were excluded based on a re-investigation of the base hydrolysis of $[Co(NH_3)_5SCN]^{2+}$ by *Buckingham* and coworkers [4], whereas strong evidence for the existence of hexacoordinated intermediates – exhibiting a lifetime of the order of ns – has been found previously [5] [6]. A substitution proceeding *via* the classical [1] pentacoordinated intermediates or just a single transition state was shown [5] [6] to be inconsistent

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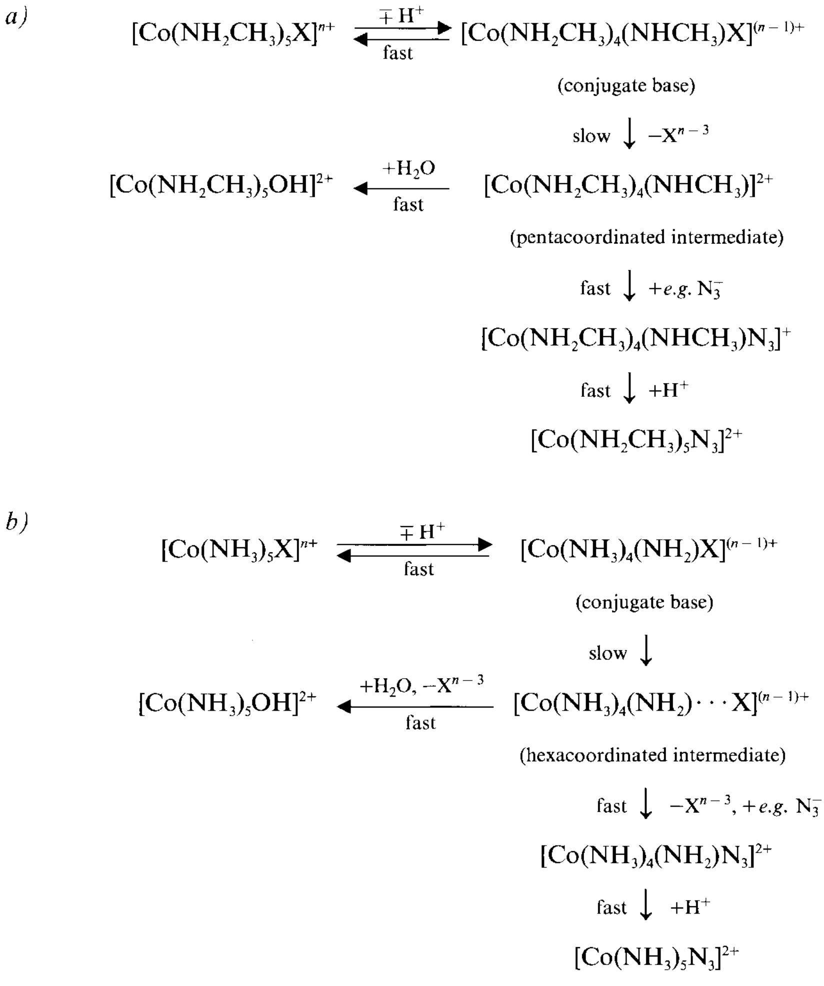
[1]) As long-lived intermediates are considered species whose lifetime is sufficiently long ($\geqslant 0.1$ ns) to allow at least a partial equilibration with its environment, *viz.* the bulk solution.

Scheme



a)

$$[\mathrm{Co(NH_2CH_3)_5X}]^{n+} \underset{\text{fast}}{\overset{\mp \mathrm{H}^+}{\rightleftarrows}} [\mathrm{Co(NH_2CH_3)_4(NHCH_3)X}]^{(n-1)+}$$

(conjugate base)

$$\text{slow} \downarrow -\mathrm{X}^{n-3}$$

$$[\mathrm{Co(NH_2CH_3)_5OH}]^{2+} \xleftarrow[\text{fast}]{+\mathrm{H_2O}} [\mathrm{Co(NH_2CH_3)_4(NHCH_3)}]^{2+}$$

(pentacoordinated intermediate)

$$\text{fast} \downarrow +e.g.\ \mathrm{N_3^-}$$

$$[\mathrm{Co(NH_2CH_3)_4(NHCH_3)N_3}]^{+}$$

$$\text{fast} \downarrow +\mathrm{H}^+$$

$$[\mathrm{Co(NH_2CH_3)_5N_3}]^{2+}$$

b)

$$[\mathrm{Co(NH_3)_5X}]^{n+} \underset{\text{fast}}{\overset{\mp \mathrm{H}^+}{\rightleftarrows}} [\mathrm{Co(NH_3)_4(NH_2)X}]^{(n-1)+}$$

(conjugate base)

$$\text{slow} \downarrow$$

$$[\mathrm{Co(NH_3)_5OH}]^{2+} \xleftarrow[\text{fast}]{+\mathrm{H_2O},\ -\mathrm{X}^{n-3}} [\mathrm{Co(NH_3)_4(NH_2)} \cdots \mathrm{X}]^{(n-1)+}$$

(hexacoordinated intermediate)

$$\text{fast} \downarrow -\mathrm{X}^{n-3},\ +e.g.\ \mathrm{N_3^-}$$

$$[\mathrm{Co(NH_3)_4(NH_2)N_3}]^{2+}$$

$$\text{fast} \downarrow +\mathrm{H}^+$$

$$[\mathrm{Co(NH_3)_5N_3}]^{2+}$$

with kinetic and competition data obtained at variable ionic strength. Pentacoordinated intermediates are formed, if strain [2] or constraints [3] are introduced into the ligand sphere – *viz.* by the use of alkylated or chelating amine ligands. The origin of the existence, lifetime, and reactivity of the intermediates is unknown at the present time, and no theoretical treatment of this problem is available from the literature. Despite of the '*trans*-effect' existing also in octahedral amine complexes of cobalt(III) [7] [8], the conjugate bases with the deprotonated amine ligand *cis* to the leaving group are believed to be the most reactive [1] ones; the origin of this apparently reversed behavior is unknown. Although base hydrolysis of amine complexes of $\mathrm{Cr^{III}}$, $\mathrm{Ru^{III}}$, $\mathrm{Rh^{III}}$, and $\mathrm{Ir^{III}}$ also exists [1], the $\mathrm{Co^{III}}$ compounds are the most reactive ones, but again, the source of this unique reactivity is unknown.

To our knowledge, no quantum mechanical calculations on the base hydrolysis have been performed thus far. In the present work, the electronic structure of the conjugate bases and possible intermediates has been investigated with SCF MS-Xα calculations. The aim of this work was to understand the base hydrolysis of (acidato)(pentaamine)cobalt(III) complexes and to predict the behavior of the much less studied analogous Cr^{III}, Ru^{III}, Rh^{III}, and Ir^{III} complexes. For this purpose, the electronic structures were correlated with the dissociative [1] activation of the leaving group (here Cl^-). The calculations allowed the rationalization of the reactivity of Co^{III} complexes and predict the nonexistence of intermediates for the base hydrolysis of amine complexes of Cr^{III}, Ru^{III}, Rh^{III}, and Ir^{III}.

Choice of an Adequate Quantum-Chemical Model. – To reach numerical accuracy (in particular for the triplet and quintet states) using state-of-art quantum-chemical techniques, MCSCF calculations using extended basis sets, followed by second-order CI, would obviously be required. Even if geometry optimization is not performed at this level, such calculations would be unduly intricate and would require a prohibitive amount of computer time. We decided, therefore, to resort to proven semi-empirical methods which generally provide a valuable basis for a meaningful discussion of the most important chemical aspects of such problems. It is indeed our opinion that the quantum-chemical model used in the present study should allow to discuss the existence of factors stabilizing the dissociative activation of the substitution process of such conjugate bases. To this end, the theoretical model should be able to lead to a general and semi-quantitative understanding of the detailed mechanism rather than predicting absolute-energy differences with the highest possible accuracy. In view of the capabilities of the semi-empirical models mostly used in inorganic chemistry, we have decided to resort to two different techniques which may be regarded as complementary: the modified extended *Hückel* method (MEHMO) introduced by *Anderson* [9–11] which has proven useful to estimate molecular geometries, and the SCF MS-Xα model which has been shown to provide semi-quantitative relative state energies. Thus, a combination of these two models has been applied to investigate and discuss the base hydrolysis reaction.

Computational Details. – *Modified Extended* Hückel *MO Calculations.* They were performed using a modified version of the program ICON 8.0 including *Anderson*'s twobody repulsion term [9–11]. The approximate optimized geometry was estimated by trial and error. Then, close to the local minimum, all the internal coordinates (bond lengths and angles) to be optimized were varied systematically in order to obtain the total energy as a function of internal coordinates. The optimized energy and internal coordinates were determined by fitting the various energies to a harmonic potential, and by setting subsequently the first derivatives (with respect to the internal coordinates) of the potential equal to zero.

The VSIE's, the single ζ's of N, H, and Cl, the A, B, C parameters and the double ζ's for Co were taken from the literature [12] [13].

SCF MS-Xα Calculations. The standard version of the SCF MS-Xα program [14] was used. The atomic exchange parameters were taken from calculations of *Schwarz* [15] [16], whereas those of the inter- and outer-sphere were determined as the valence-electron-weighted average of all the atomic parameters. The atomic sphere radii were obtained nonempirically based on the criteria of *Norman* [17]. The thus determined radii for the same type of atoms were averaged and then reduced in order to realize a 10% overlap of the M and N spheres. In the intermediates with elongated Co–N bonds, the 10% overlap was based on the shorter (equatorial) Co–N bonds exclusively, *i.e.* the Co and N spheres of elongated Co–N bonds did not even touch each other. A tangent outer-sphere and a *Watson* sphere with the same radius bearing the counter charge was used. For the outer-sphere and the Cr, Co, Rh, Cl, N, and H atoms, respectively, wavefunctions with l values up to 4, 2, 2, 2, 2, 1, an 0, respectively, were used.

In most of the complexes calculated, the lone pair of the NH_2^- ligand was found to be very diffuse, *viz.* > 20% of its charge was located in the inter-sphere region. In some of these cases, a pair of empty spheres (with $r_{ES} = 0.75 \cdot r_N$, 25% overlap) lying above and below the NH_2^- plane were introduced. This did not alter the orbital energies significantly, but showed where the inter-sphere charge was located. All the singlet-triplet and triplet-quintet splittings (*Table 1*) were calculated using the transition state theory [18].

Atomic coordinates (x, y, z), sphere radii (r), and exchange parameter values (α) for all the calculated complexes are available from the authors on request.

Results. – Base hydrolysis of (acidato)(pentaamine) complexes of Co^{III} (*Scheme*) will be discussed first, because the latter are the most extensively [1–6] studied compounds. The conjugate base is at least six orders of magnitude more reactive [1] than the protonated species, therefore, its electronic structure is expected to reveal some information on its enhanced reactivity. The calculations will show that the key feature of the more reactive *cis*-isomer is a small HOMO – LUMO gap being responsible for the small singlet-triplet energy difference (*Table 1*). In a second set of calculations, the electronic structure of conjugate bases exhibiting activated Co–Cl bonds will be calculated. The activated conjugate base *cis*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ is identical with the hexacoordinated intermediate [6] and exhibits an electronic triplet ground state. Then, electronic structures of pentacoordinated intermediates [2] [3] will be compared with those of the hexacoordinated [6] ones. The results of the present calculations allow to discuss the reaction coordinate of the alkaline hydrolysis of amine complexes of Co^{III} and finally, predictions for the corresponding reactivity of compounds involving inert transition metals other than Co^{III} are made.

Table 1. *Triplet and Quintet Energies Relative to the Singlet State*[a])

Compound	Geometry	Triplet	Quintet
cis-$[Co(NH_3)_4(NH_2)Cl]^+$	octahedral	1.35	2.80
trans-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$	elongated octahedral	0.65[b])	–
trans-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$	elongated octahedral	0.51[c])	–
cis-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$	elongated octahedral	−0.18	1.54
apical-$[Co(NH_3)_4(NH_2)]^{2+}$	square-pyramidal	0.40	–
basal-$[Co(NH_3)_4(NH_2)]^{2+}$	square-pyramidal	0.46	–
equatorial-$[Co(NH_3)_4(NH_2)]^{2+}$	trigonal-bipyramidal	−0.11	1.57
equatorial-$[Rh(NH_3)_4(NH_2)]^{2+}$	trigonal-bipyramidal	0.16	–

[a]) Energies in eV. [b]) Shorter axial bonds. [c]) Longer axial bonds.

The geometries of the hexacoordinated intermediates (*Table 2*) have been estimated using the MEHMO method, and all the electronic structures reported in this work have

Table 2. *Bond Lengths*[a]) *of the Investigated Compounds*

	M–Cl	M–N	Reference
$[Co(NH_3)_5Cl]^{2+}$	2.286	1.973	[19]
	2.20	2.01	this work[b])
$[Cr(NH_3)_5Cl]^{2+}$	2.327	2.074	[20]
$[Rh(NH_3)_5Cl]^{2+}$	2.355	2.076	[21]
cis-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$	2.59	1.973[c]), 2.39[d])	this work[b])
trans-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$	2.60	1.973[c]), 2.26[d])	this work[b])
	2.68	1.973[c]), 2.35[d])	this work[e])

[a]) Units are Å. [b]) Calculated using the first set of VSIE's; see text. [c]) Co–N bonds *cis* to Cl^- (not optimized). [d]) Co–N bond *trans* to Cl^- (optimized). [e]) Calculated using the second set of VSIE's; see text.

been calculated using the spin-polarized SCF MS-Xα model. Relative state energies for all the conjugate bases and intermediates of interest have been determined (*Table 1*) in order to examine, whether a dissociative activation of the conjugate base leads to a stabilization of the electronic structure *via* a spin-multiplicity change.

Conjugate Base cis-*$[Co(NH_3)_4(NH_2)Cl]^+$*. Currently, it is accepted [1] to be more reactive, and hence also more interesting, than its *trans*-isomer. Unfortunately, the X-ray crystal structure [7] of the constrained conjugate base [Co(dinosar – H)]$^{2+}$ – a hexaamine complex where formation of a planar deprotonated amine is impossible – is not representative for the conjugate bases of acidato-pentaamine complexes of Co^{III}. Due to the absence of pertinent structural information, the geometries of the conjugate bases were approximated by those of the corresponding $[M(NH_3)_5Cl]^{2+}$ complexes (*Table 2*).

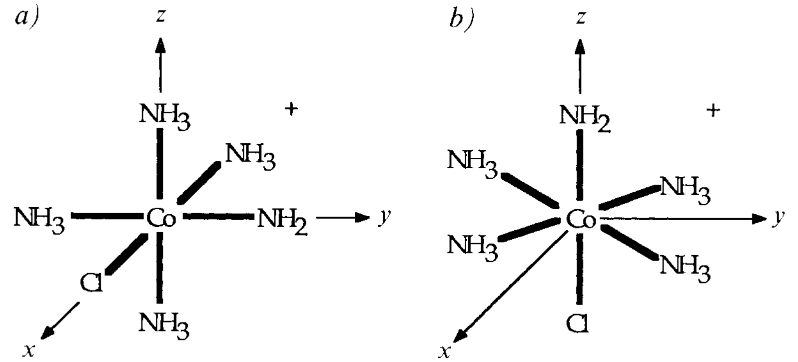


Fig. 1. a) *Coordinate system of* cis-*$[Co(NH_3)_4(NH_2)Cl]^+$ or* cis-*$[Co(NH_3)_4(NH_2)\cdots Cl]^+$*. b) *Coordinate system of* trans-*$[Co(NH_3)_4(NH_2)Cl]^+$ or* trans-*$[Co(NH_3)_4(NH_2)\cdots Cl]^+$*

The orientation of *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ in the coordinate system is represented in *Fig. 1a*. Because of the low symmetry (C_s) giving rise to only two irreducible representations, it is convenient to describe the relevant upper MO's with respect to the axis of the coordinate system.

The electronic structure was calculated using the SCF MS-Xα model. The 19a′ and 18a′ levels are the metal-centered antibonding d_{σ^*} orbitals (*Fig. 2a* and *Table 3*). Interest-

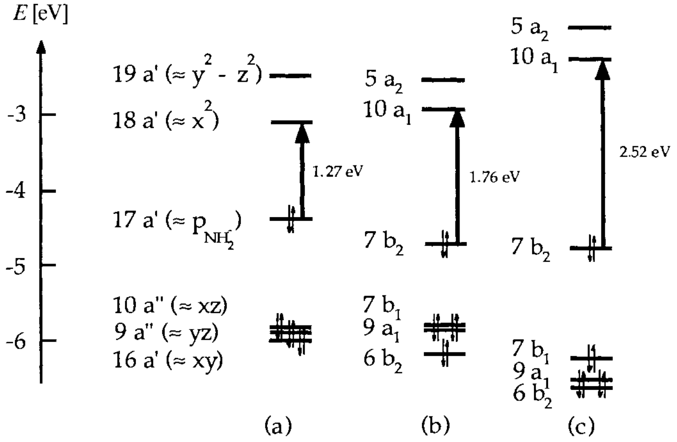


Fig. 2. *Upper valence MO's of conjugate bases:* a) cis-$[Co(NH_3)_4(NH_2)Cl]^+$, b) trans-$[Co(NH_3)_4(NH_2)Cl]^+$, *and* c) trans-$[Rh(NH_3)_4(NH_2)Cl]^+$

Table 3. *Valence Molecular Orbitals of the Conjugate Base* cis-$[Co(NH_3)_4(NH_2)Cl]^+$

Level[a]	Energy[b]	Co	Cl	N1[c]	N2[d]	H[e]	ES[f]	INT[g]	OUT[h]
19a′*	−2.47	59	0	19	10	2	0	7	2
18a′*	−3.09	59	14	18	10	1	0	5	2
17a′	−4.36	16	2	1	52	0	14	13	1
10a″	−5.80	85	9	0	0	1	0	4	0
9a″	−5.89	94	0	1	0	2	0	3	0
16a′	−5.99	63	21	1	7	1	1	7	1
8a″	−7.19	10	71	6	0	1	0	12	1
15a′	−7.20	16	40	10	17	3	1	12	1
14a′	−7.72	13	50	14	11	3	0	7	2
13a′	−7.98	12	39	11	3	4	2	11	1
7a″	−8.51	10	5	66	0	6	0	13	1
12a′	−9.58	38	4	45	3	4	0	6	0
11a′	−9.78	38	2	45	3	5	0	6	0
10a′	−10.57	20	5	51	3	7	0	13	1
6a″	−12.07	1	0	3	52	44	0	0	0
5a″	−13.83	0	0	57	0	42	0	0	0
9a′	−13.92	0	0	58	0	42	0	0	0
4a″	−13.95	0	0	57	1	42	0	0	0
8a′	−14.16	0	1	57	0	41	0	0	0
7a′	−14.21	0	0	57	0	42	0	0	0
3a″	−14.56	1	0	57	0	41	0	0	0
6a′	−14.66	1	0	57	0	42	0	0	0
2a″	−14.82	1	0	56	0	42	0	0	0
5a′	−18.86	2	93	0	1	1	0	3	0
4a′	−20.04	2	1	0	67	26	4	0	0
3a′	−24.13	1	0	67	0	32	0	0	0
1a″	−24.19	1	0	67	0	32	0	0	0
2a′	−24.22	1	0	67	0	32	0	0	0
1a′	−24.58	2	0	66	0	32	0	0	0

[a] Doubly occupied orbitals; those denoted with a * are empty. [b] In eV. [c] NH_3 ligands. [d] NH_2^- ligand. [e] All H-atoms. [f] Empty spheres positioned on the axis of the lone pair of the NH_2^- ligand. [g] Inter-sphere. [h] Outer-sphere.

ingly, the HOMO 17a′ represents the lone pair of the NH_2^- ligand; the metal-centered d_π orbitals 10a″, 9a″, and 16a′ lie far below and, therefore, the NH_2^- ligand is much more reducing than the NH_3 ligands. The small HOMO – LUMO gap of 1.27 eV is unique to (acidato)(pentaamine)cobalt(III) complexes with the deprotonated amine ligand in *cis*-position to the leaving group and much smaller than the crystal-field-splitting parameter of ~ 3 eV, generally observed in amine complexes of Co^{III}. As a consequence, the corresponding singlet-triplet gap is small, but the quintet state lies far above the singlet one (*Table 1*). Small bond length changes, *viz.* shortening of the $Co-NH_2$ bond by $\leqslant 0.04$ Å and elongation of the Co–Cl one by $\leqslant 0.1$ Å are not expected to alter the sequence of the state levels (a slight stabilization of the 18a′ and a slight destabilization of the 19a′ levels would take place). It will be shown that the small HOMO – LUMO gap of 1.27 eV is likely to be responsible for the unique reactivity of this conjugate base, since a dissociative activation of the Co–Cl bond will stabilize the 18a′ level, and the 17a′–18a′ gap gets sufficiently small that the triplet electron configuration becomes the ground state of the hexacoordinated intermediate.

Table 4. *Valence Molecular Orbitals of the Conjugate Base* trans-*$[Co(NH_3)_4(NH_2)Cl]^+$*

Level[a])	Energy[b])	Co	Cl	N1[c])	N2[d])	H[e])	ES[f])	INT[g])	OUT[h])
$5a_2$*	−2.57	62	0	29	0	0	0	7	2
$10a_1$*	−2.94	56	12	8	13	2	0	6	2
$7b_2$	−4.71	26	1	1	47	0	12	11	1
$7b_1$	−5.78	86	8	0	0	1	0	4	0
$9a_1$	−5.86	94	0	1	0	2	0	3	0
$6b_2$	−6.18	58	10	3	16	1	4	8	0
$6b_1$	−7.39	8	67	10	0	1	0	12	1
$5b_2$	−7.44	11	66	7	1	1	0	12	1
$8a_1$	−7.52	8	50	1	26	5	0	7	2
$5b_1$	−8.40	10	10	60	0	6	0	13	1
$4b_2$	−8.46	9	9	61	1	5	0	14	1
$7a_1$	−9.12	42	24	4	23	4	0	2	1
$4a_2$	−9.80	41	0	48	0	4	0	6	0
$6a_1$	−10.51	21	5	51	3	7	0	13	0
$4b_1$	−12.50	0	0	7	49	44	0	0	0
$3a_2$	−13.40	0	0	58	0	42	0	0	0
$2a_2$	−13.75	0	0	58	0	42	0	0	0
$3b_2$	−13.91	1	0	58	0	41	0	0	0
$3b_1$	−13.94	1	0	55	2	41	0	0	0
$5a_1$	−14.09	0	1	56	1	41	0	0	0
$2b_2$	−14.14	1	0	57	0	42	0	0	0
$2b_1$	−14.21	1	0	54	2	42	0	0	0
$4a_1$	−14.66	2	0	57	0	42	0	0	0
$3a_1$	−19.08	2	94	0	0	0	0	3	0
$2a_1$	−20.54	1	0	0	67	27	4	0	0
$1a_2$	−23.83	1	0	67	0	33	0	0	0
$1b_2$	−23.96	1	0	67	0	33	0	0	0
$1b_1$	−23.97	1	0	67	0	33	0	0	0
$1a_1$	−24.28	2	0	66	0	32	0	0	0

[a]) Doubly occupied orbitals; those denoted with a * are empty. [b]) In eV. [c]) NH_3 ligands. [d]) NH_2^- ligand. [e]) All H-atoms. [f]) Empty spheres positioned on the axis of the lone pair of the NH_2^- ligand. [g]) Inter-sphere. [h]) Outer-sphere.

Conjugate Bases trans-*[M(NH$_3$)$_4$(NH$_2$)Cl]$^+$*. To make the four equatorial NH$_3$ ligands equivalent in C_{2v} symmetry, the x and y axis of the coordinate system (*Fig. 1b*) were chosen to bisect the H$_3$N–M–NH$_3$ angles. The NH$_2^-$ and Cl$^-$ ligands were placed on the z axis.

The results of the SCF MS-Xα calculation for M = Co are presented in *Fig. 2b* and *Table 4*. This electronic structure is similar to that of the *cis*-isomer (the virtual 5a$_2$ and 10a$_1$ levels are the antibonding metal-centered d$_{\sigma*}$ orbitals, the HOMO 7b$_2$ is the lone pair of the NH$_2^-$ ligand and lies above the nonbonding metal-centered 7b$_1$, 9a$_1$, and 6b$_2$ orbitals d$_\pi$). The HOMO – LUMO gap is also small (1.76 eV), but considerably larger (by 0.49 eV) than those of the corresponding *cis*-isomer.

The conjugate base *trans*-[Rh(NH$_3$)$_4$(NH$_2$)Cl]$^+$, valence isoelectronic with the corresponding Co^{III} analog, exhibits qualitatively the same electronic structure (*Fig. 2c*). The larger crystal field splitting parameter of second-row transition metals is responsible for the considerably larger HOMO – LUMO gap of 2.52 eV.

The analogues Cr^{III} compound exhibits a half filled d$_\pi$ shell (6b$_2$↑, 9a$_1$↑, 7b$_1$↑) in contrast to the corresponding Rh^{III} and Co^{III} complexes. The upper molecular orbitals of the ^{4}A$_2$ ground state – obtained from a spin-polarized calculation – are presented in *Table 5*. A dissociative activation of the Cr–Cl bond is expected to stabilize the empty 10a$_1$↑ orbital by about 1.0–1.5 eV at most (by comparison to the corresponding stabilization observed for complexes with a low spin Co^{III} center, see below). Since this level will neither cross nor come close to any of the occupied spin-orbitals, a dissociative activation is unlikely to be accompanied by a stabilization of the electronic structure2).

Table 5. *Upper Valence Molecular Orbitals of the Conjugate Base* trans-*[Cr(NH$_3$)$_4$(NH$_2$)Cl]$^+$*

Levela)	Energyb)	Cr	Cl	N1c)	N2d)	He)	ESf)	INTg)	OUTh)
6b$_2$↓*	–2.41	82	3	0	5	1	1	6	1
5a$_2$↑*	–2.58	64	0	28	0	1	0	6	1
9a$_1$↓*	–2.61	92	0	0	0	2	0	6	0
7b$_1$↓*	–2.64	89	3	0	0	1	0	6	0
10a$_1$↑*	–2.79	57	14	9	12	1	0	5	2
7b$_2$↑	–4.64	26	2	1	48	0	12	11	1
7b$_2$↓	–5.28	7	1	2	60	0	15	14	1
7b$_1$↑	–5.73	81	12	0	0	1	0	5	0
9a$_1$↑	–5.87	94	0	1	0	2	0	4	0
6b$_2$↑	–6.14	52	15	2	16	1	4	8	1

a) Singly occupied spin orbitals; those denoted with a * are empty. b) In eV. c) NH$_3$ ligands. d) NH$_2^-$ ligand. e) All H-atoms. f) Empty spheres positioned on the axis of the lone pair of the NH$_2^-$ ligand. g) Inter-sphere. h) Outer-sphere.

Hexacoordinated Intermediates cis- *and* trans-*[Co(NH$_3$)$_4$(NH$_2$)$\cdots$Cl]$^+$*. Since there is strong evidence [5] [6] for the existence of at least one of the isomers, it is worthwhile to discuss their electronic structures in detail. The coordinate system was chosen as for the corresponding conjugate bases (*Fig. 1*). The geometries (*Table 2*) were computed using the MEHMO method based on the hypothesis (which will be analyzed critically later)

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2) The same prediction is expected to be valid for the corresponding *cis*-isomer exhibiting a HDOMO-LUMO gap of 2.1 eV.

that the intermediates exhibit a triplet electron configuration. The Co—N bond lengths *cis* to the Cl^- ligand were chosen to be the same as those of $[Co(NH_3)_5Cl]^{2+}$, the Co—Cl and the *trans*-Co—N bonds were optimized as described (*cf. Computational Details*). To check the accuracy of the MEHMO method, we have calculated the Co—NH_3 and Co—Cl bond lengths of $[Co(NH_3)_5Cl]^{2+}$; they were reproduced within a 5% accuracy (*Table 2*). Furthermore, geometries and activation energies of first-row transition-metal carbonyl complexes have been predicted [22] [23] successfully using the same technique.

For *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$, two sets of MEHMO calculations were performed (*Table 2*): in the first one, the VSIE's of Co were determined from self-consistent charge calculations (SCCC) based on $[Co(NH_3)_5Cl]^{2+}$. The thus obtained VSIE's of Co (3d: – 13.00; 4s: –10.08; 4p; –5.40 eV), which were also used to calculate the Co—N and Co—Cl bond lengths of $[Co(NH_3)_5Cl]^{2+}$ (see above), gave rise to shorter axial bond lengths (*Table 2*). Although the calculated axial bond lengths appear reasonable, the sequence of the orbitals was questionable, since the lone pair of NH_2^- which should be the HOMO (see below) was predicted to lie below the Co d_π levels. To obtain a correct sequence of the orbitals, a second calculation was performed. This time, the VSIE's of the Co center and the NH_2^- nitrogen were determined by SCCC based on the conjugate base (Co: 3d: –12.26; 4s: –9.66; 4p: –5.09. N: 2s: –22.61; 2p: –10.78 eV), and the MEHMO calculations gave rise to longer axial bond lengths (*Table 2*). To prevent a preference of the triplet by choosing the VSIE's leading to longer axial bond lengths, the geometry of the *cis*-isomer was determined as described above using the first set of VSIE's. It should be noted that the Co—NH_3 bond *trans* to the Co—Cl one is significantly longer than the Co—NH_2 one.

The SCF MS-Xα calculations show that the triplet state of the *trans*-isomer has a higher energy than the singlet one (*Table 1*), although the HOMO – LUMO gap in the singlet (*Fig. 3a*) has decreased by almost 1 eV compared to that of the corresponding

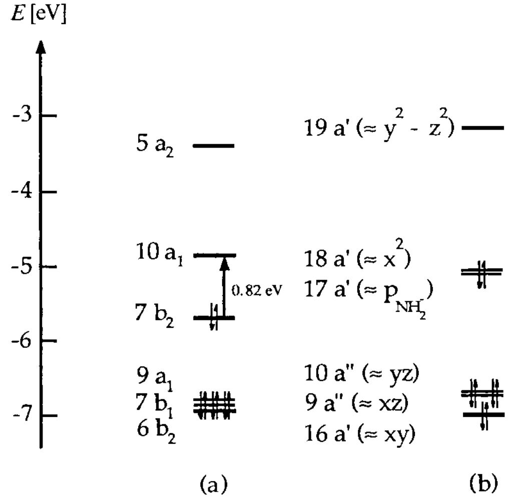

Fig. 3. *Upper valence MO's of hexacoordinated intermediates:* a) trans-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ *and* b) cis-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$

conjugate base. Also for the geometry based on the second set of MEHMO calculations having yield longer axial bonds, the triplet energy is still higher than that of the singlet one (*Table 1*). In spite of the uncertainties in the geometry, there is no doubt that the singlet state, which is not in its equilibrium geometry in this case, is nevertheless more stable than the triplet. This means that the hexacoordinated intermediate *trans*-$[Co(NH_3)_4(NH_2) \cdots Cl]^+$ exists only as an excited state which is not accessible in a thermal reaction. The singlet state in its equilibrium geometry is of course identical with the conjugate base.

Table 6. *Valence Molecular Orbitals of the Hexacoordinated Interemediate* cis-$[Co(NH_3)_4(NH_2) \cdots Cl]^+$

Level[a])	Energy[b])	Co	Cl	N1[c])	N2[d])	H[e])	INT[f])	OUT[g])
19a′*	−3.17	59	0	23	8	1	8	1
18a′*	−5.10	55	17	13	7	1	7	1
17a′	−5.12	22	1	5	49	0	23	0
10a″	−6.67	94	0	1	0	2	3	0
9a″	−6.71	90	5	1	0	1	4	0
16a′	−6.98	63	20	1	7	0	8	0
8a″	−7.67	5	81	2	0	1	11	1
15a′	−7.71	7	66	11	2	1	12	1
14a′	−7.96	12	49	16	6	2	15	1
13a′	−8.64	17	7	28	27	7	14	0
12a′	−8.72	26	18	32	6	4	14	1
7a″	−8.82	11	2	67	0	6	15	0
11a′	−10.38	43	0	35	10	5	6	0
10a′	−10.97	25	1	44	9	7	14	0
6a″	−13.47	0	0	13	43	43	0	0
5a″	−14.07	0	0	57	0	42	0	0
9a′	−14.09	0	0	58	0	42	0	0
4a″	−14.17	0	0	51	7	42	0	0
8a′	−14.26	0	0	58	0	42	0	0
7a′	−14.38	0	0	58	0	41	0	0
3a″	−14.49	1	0	56	1	41	0	0
6a′	−14.58	1	0	57	0	42	0	0
2a″	−15.01	2	0	54	3	42	0	0
5a′	−19.24	0	96	0	0	0	3	0
4a′	−21.48	2	0	0	70	28	0	0
3a′	−24.08	0	0	67	0	32	0	0
2a′	−24.32	1	0	67	0	31	0	0
1a″	−24.37	1	0	67	0	32	0	0
1a′	−24.64	2	0	67	0	31	0	0

[a]) Doubly occupied orbitals; those denoted with a * are empty. [b]) In eV. [c]) NH_3 ligands. [d]) NH_2^- ligand. [e]) All H-atoms. [f]) Inter-sphere. [g]) Outer-sphere.

For the *cis*-isomer with the approximate equilibrium geometry of the triplet obtained by the first set of MEHMO calculations (shorter axial bonds which are less favorable to triplet formation) a HOMO – LUMO (18a′–17a′) gap of only 0.03 eV was calculated (*Fig. 3b*, *Table 6*). Remarkably, for this isomer the triplet state is more stable (*Table 1*) than the singlet (which again, is not in its equilibrium geometry). *Not the magnitude of this energy gap is relevant – it depends on the estimated geometry anyway – but the fact that for a given elongation of the Co–Cl bond the triplet state is more stable than the singlet.* This is only possible for the present case. The quintet state lies far above the triplet, and it is thus disregarded (*Table 1*). The triplet state is best represented as a (low-spin) *cis*-$[Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl]^+$ complex, since the spin-polarized calculations showed that approximately one unpaired spin is located on the Co center (18a′↑ level) and the other one mainly on the NH_2^- ligand (17a′↑ level).

Pentacoordinated Intermediates. Since their Co–N bond lengths are unknown, they were also taken to be equal to those of $[Co(NH_3)_5Cl]^{2+}$. For a *qualitative* discussion of the relevant electronic states, this approximation is certainly justified. The electronic structure of square pyramidal *apical*-$[Co(NH_3)_4(NH_2)]^{2+}$ (*Fig. 4a*) resembles those of the hexacoordinated intermediate *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ (*Fig. 3a*) very much: the HOMO $6b_2$ again is the lone pair of the NH_2^- ligand. The HOMO – LUMO gap is 0.89 eV, and like *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$, the ground state is a singlet; the triplet is an excited state (*Table 1*). The ground state of the corresponding basal isomer with C_S symmetry is also a singlet (*Table 1*); thus, both the square pyramidal isomers – like [24] $[Co(en)_2CN]^{2+}$ and $[Co(en)_2OH]^{2+}$ (en = 1,2-ethanediamine) – exhibit singlet electronic ground states. It is obvious that a slight elongation of the apical Co–N bond would stabilize the triplet state, but then, the total energy of the (already coordinatively unsaturated) pentacoordinated intermediate is likely to increase. In spite of the geometrical uncertainties, these triplets are expected to be excited states as that of the hexacoordinated intermediate *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$, and, therefore, square-pyramidal intermediates are unlikely to be formed. The present electronic structures are only interesting in comparison with those of trigonal bipyramidal intermediates (*Fig. 4*).

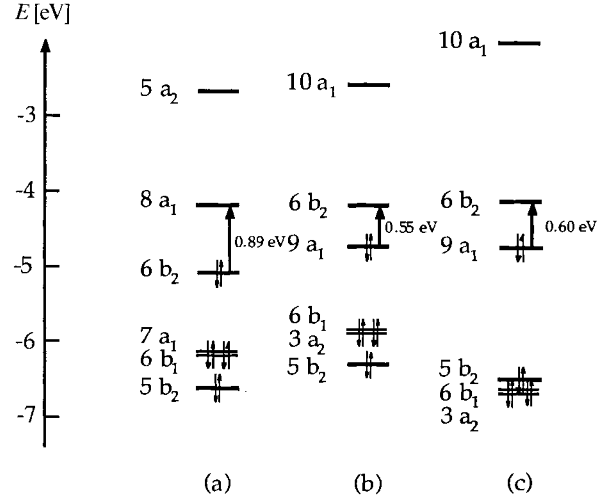

Fig. 4. *Upper valence MO's of pentacoordinated intermediates:* a) *square-pyramidal* apical-$[Co(NH_3)_4(NH_2)]^{2+}$, b) *trigonal-bipyramidal* equatorial-$[Co(NH_3)_4(NH_2)]^{2+}$, *and* c) *trigonal-bipyramidal* equatorial-$[Rh(NH_3)_4(NH_2)]^{2+}$

Although, on a superficial view, trigonal bipyramidal *equatorial*-$[Co(NH_3)_4(NH_2)]^{2+}$ (Co–N bond lengths as in $[Co(NH_3)_5Cl]^{2+}$) with C_{2v} symmetry appears to exhibit an electronic structure (*Fig. 4b*) very similar to that of the previously calculated intermediates, it is quite different. The HOMO – LUMO gap is slightly smaller (0.55 eV), but – in contrast to the previous cases – the lone pair of the NH_2^- ligand ($5b_2$) lies below the (nonbonding) metal-centered d_π levels ($3a_2$, $6b_1$, and $9a_1$). The triplet ground state is more stable than the quintet and singlet states (*Table 1*). The two unpaired spins of the triplet are both localized mainly on the Co center ($6b_2\uparrow$ and $9a_1\uparrow$ levels; *Fig. 4b*); this intermediate is best described as a Co^{III} complex with two unpaired spins on the metal center in contrast to the triplet of *cis*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ which is biradical.

With the exception of the larger splittings due to the increased crystal-field strength of second-row transition metals, the electronic structure of trigonal bipyramidal *equatorial*-$[Rh(NH_3)_4(NH_2)]^{2+}$ (*Fig. 4c*) resembles that of the corresponding valence isoelectronic Co^{III} analog (*Fig. 4b*) very much. However, here the triplet state is less stable than the singlet (*Table 1*).

Discussion. – The electronic structures presented show three striking features: *i*) in all the conjugate bases calculated using the Xα model, the HOMO represents the lone pair of the NH_2^- ligand; *ii*) the far smallest HOMO – LUMO gap among the conjugate bases is found for *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$; *iii*) two of the calculated intermediates, namely *cis*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ and *equatorial*-$[Co(NH_3)_4(NH_2)]^{2+}$, exhibit ground states with a different spin multiplicity than their conjugate base precursors. These three features are related to each other, since the small HOMO – LUMO gap of the conjugate base *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ – which is due to the quite high-lying energy of the NH_2^- lone pair – favors the stabilization of the electronic structure during the formation of the intermediate by crossing into a triplet state. Consequently, the substitution reaction base hydrolysis is accompanied by spin changes, if the metal center is Co^{III}.

Reaction Coordinate. The singlet electronic ground state of *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ at its equilibrium geometry is identical with the conjugate base. For this geometry, the triplet is less stable (*Table 1*). The triplet electronic ground state of *cis*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ at its equilibrium geometry – exhibiting elongated Co–Cl and *trans*-Co–N bonds – is identical with the hexacoordinated intermediate. For this geometry, however, the singlet is less stable (*Table 1*). Therefore, the singlet and triplet potential-energy surfaces of conjugate base and hexacoordinated intermediate, respectively, cross each other (*Fig. 5*), and a dissociative activation of the conjugate base *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ leads to the corresponding hexacoordinated intermediate which is a stable species [6] exhibiting a triplet electronic ground state. The existence of this species obviously lowers the energy of activation for a dissociative substitution which would follow otherwise the $^1A'$ potential-energy surface further, until the interchange process interferes. The facile formation of the hexacoordinated intermediate can also be visualized by inspection of the electronic structure of the conjugate base (*Fig. 2a*, *Table 1*): a dissociative activation stabilizes the LUMO 18a′. Once the HOMO – LUMO (17a′–18a′) gap is sufficiently small, the electronic structure is stabilized by the transfer of a 17a′ electron into the 18a′ orbital. In fact, for the hexacoordinated intermediate in its singlet state the 17a′ and 18a′ levels are almost isoenergetic (*Fig. 3b*, *Table 6*).

Strain or constraints in the ligand sphere favor the formation of pentacoordinated intermediates [2] [3] which are, however, always preceded by an activated hexacoordinated species with a triplet electron configuration. Since no electronic stabilization is possible in the square-pyramidal intermediates, only the trigonal bipyramidal intermediate *equatorial*-$[Co(NH_3)_4(NH_2)]^{2+}$ is of interest. Also for this species, the electronic singlet state lies higher than the triplet $^3B_2$ (*Table 1*). The relative energies of the $^3A'$ and $^3B_2$ states (*Fig. 5*) are expected to depend mainly on the nature of the amine ligands; for the $[Co(NH_3)_5X]^{n+}$ systems, the hexacoordinated intermediate with a $^3A'$ state is more stable than the trigonal-bipyramidal one exhibiting a $^3B_2$ state, or the energy of activation for the formation of the trigonal bipyramid is higher than that required for product formation *via* the hexacoordinated intermediate, since no contribution of pentacoordinated intermediates to the product formation has been detected [5] [6]. In the *mer*-[Co(dien)(dapo)X]$^{n+}$ system [3], however, product formation occurs exclusively *via* a trigonal bipyramid. In this case, its $^3B_2$ state is likely to be more stable than the $^3A'$ one. *Fig. 5* shows clearly that the energy of activation for the formation a trigonal bipyramid is determined by the $^3A'$ potential-energy surface of the hexacoordinated intermediate or transition state. It is obvious that in the absence of the $^3A'$ potential-energy surface the energy of activation for a dissociative substitution is considerably higher. Base hydrolysis of $[Co(NH_2CH_3)_5X]^{n+}$ also proceeds [2] *via* a pentacoordinated intermediate, but its geometry was not determined.

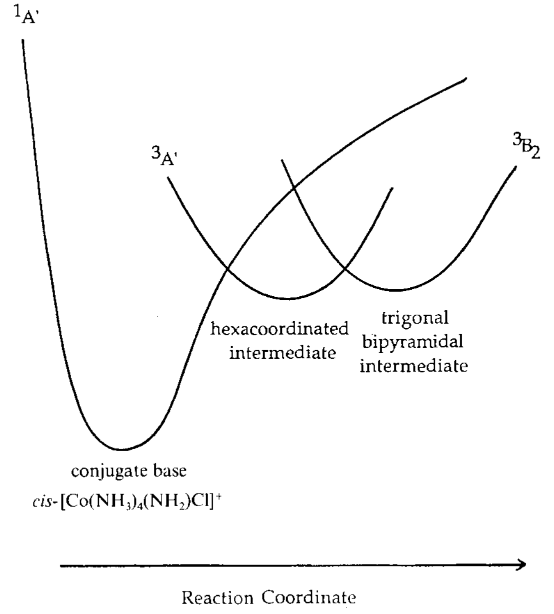

Fig. 5. *Qualitative potential-energy surface for the reaction of the conjugate base* cis-$[Co(NH_3)_4(NH_2)Cl]^+$. The reaction coordinate is the elongation of the Co–Cl bond. During formation of the hexacoordinated intermediate the Co–N bond *trans* to Cl^- is also elongated (*Table 2*), but it is shortened again, when formation of the trigonal bipyramid takes place.

A complete dissociation of the leaving group from the conjugate base *trans*-$[Co(NH_3)_4(NH_2)Cl]^+$ would lead to a pentacoordinated species, *e.g.* *equatorial*-

$[Co(NH_3)_4(NH_2)]^{2+}$. Since the $^1A_1$ state of this trigonal bipyramidal species is an excited state (*Table 1*), the potential-energy surface of its triplet ground state ($^3B_2$) crosses the $^1A_1$ potential-energy surface of the conjugate base (*Fig. 6*). In contrast to the *cis*-isomer, the $^3B_2$ state of the hexacoordinated intermediate *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ is an excited state (*Table 1*). Therefore, its potential-energy surface does not cross that of the conjugate base and, as a consequence, dissociative activation of the latter does not lead to a stable hexacoordinated intermediate (*Fig. 6*). Thus, formation of the trigonal-bipyramidal intermediate would occur *via* a 'late' and, therefore, unfavorable, transition state in contrast to the corresponding transformation of *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ (*Fig. 5*). Most likely, a concerted substitution mechanism is preferred over the formation of a pentacoordinated intermediate *via* an unfavorable 'late' transition state. In other words, formation of a pentacoordinated intermediate appears only possible, if a stable hexacoordinated species exists as a precursor (*Figs. 5* and *6*).

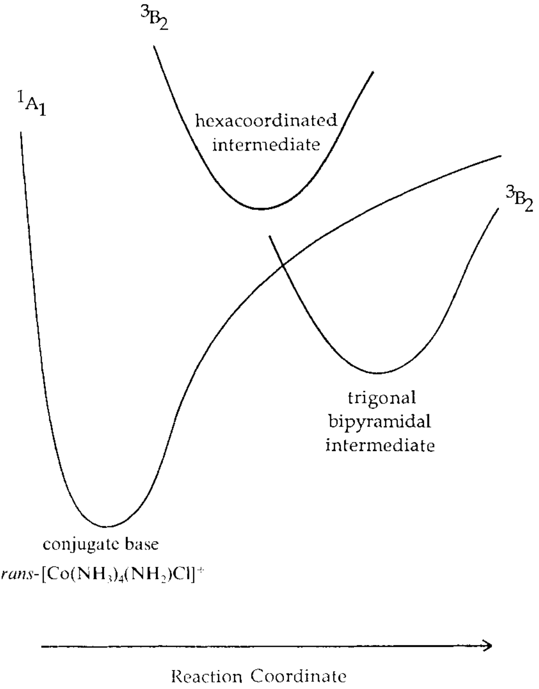

Fig. 6. *Qualitative potential-energy surface for the reaction of the conjugate base* trans-$[Co(NH_3)_4(NH_2)Cl]^+$. The reaction coordinate is the elongation of the Co–Cl bond.

In general, hexacoordinated intermediates (with a stabilized electronic structure) exist, if – along with the dissociative activation – the population of an empty d_{σ^*} MO by a HOMO electron is a favorable process. A sufficiently small HOMO – LUMO gap and a doubly occupied HOMO in the prescursor (conjugate base) to the intermediate are required. These conditions are met for the conjugate base *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$, but not for *trans*-$[Co(NH_3)_4(NH_2)Cl]^+$ and the corresponding *cis*- or *trans*-analogues of Cr^{III}, Ru^{III}, Rh^{III}, and Ir^{III}, where the HOMO is occupied by a single electron (Cr^{III} and Ru^{III} exhibit a partially filled d_π shell), or the HOMO – LUMO gap is too large (the second- and third-row transition metals Ru^{III}, Rh^{III}, and Ir^{III} exhibit a too large crystal-field splitting parameter).

Consistency with the Literature. The transformation of the conjugate base *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ into its corresponding hexacoordinated intermediate resembles the $^3T_{1g} \leftarrow {}^1A_{1g}$ excitation of $[Co(NH_3)_6]^{3+}$ very much, because in the $^3T_{1g}$ state of the latter, two axial bonds are elongated by ~ 0.12 Å [25]. The crystal field splitting parameter Δ or 10 Dq – being identical to the HOMO – LUMO gap – is 2.98 eV [25]. Since the HOMO – LUMO gap of the conjugate base *cis*-$[Co(NH_3)_4(NH_2)Cl]^+$ is considerably smaller (by 1.71 eV), it is not surprising that a dissociative activation of the conjugate base leads to the corresponding hexacoordinated intermediate exhibiting a triplet electronic ground state (*Fig. 5*). In all the other conjugate bases, the HOMO – LUMO gaps are larger, and a dissociative activation is not accompanied by a stabilization of the electronic structure (*Fig. 6*).

Complexes of Co^{III} exhibiting a triplet electronic ground state like the hexacoordinated intermediates *cis*-$[Co(NH_3)_4(NH_2)\cdots X]^{(n-1)+}$ are not unique: the square planar $[Co^{III}L]^-$ complex [26] (L is a tetradentate N_2O_2 chelating ligand [26]) in its crystalline state and in aprotic solvents as well also exhibits a triplet electronic ground state. In aqueous pyridine, however, two pyridine molecules occupy the axial positions, and the ground state is a singlet. A spin change occurs, when the axial pyridine ligands are removed; a similar process happens in the activation of the conjugate base.

The electronic-structure calculations on the various Co^{III} complexes allow a more detailed understanding of the base hydrolysis: the lifetime [6] of the hexacoordinated intermediates *cis*-$[Co(NH_3)_4(NH_2)\cdots X]^{(n-1)+}$ is of the order of ns and most likely, this is due to the known lability of the low-spin Co^{II} center. (The analysis of spin densities showed that the hexacoordinated intermediate is best described as a low-spin *cis*-$[Co^{II}(NH_3)_4(NH_2^\bullet)\cdots Cl]^+$ complex, see previous *Sect.*) Other low-spin Co^{II} complexes show a similar reactivity, *viz.* the labile axial H_2O ligands of low-spin Co^{II} complexes containing macrocyclic tetraaza ligands are exchanged [27] within about 10 ns. The possibility, that a low-spin $Co^{II}{-}N^\bullet R_2$ species could account for the high lability of the conjugate base has already been mentioned [28], but never investigated.

Strong electron donors (like *e.g.* NH_2^-) usually labilize the ligand in *trans*-position – this is known as the '*trans*-effect' [7] [8] [29]. This principle is violated in the base hydrolysis of amine complexes of Co^{III}, because the intermediate *trans*-$[Co(NH_3)_4(NH_2)\cdots Cl]^+$ is unlikely to be formed in a thermal reaction, since it is an excited state (see previous *Sect.*). The *cis*-isomer, however, is predicted to be stable (*Table 1*) and accessible *via* a thermal activation of the conjugate base.

The ligands OH^- or H_2O do not exert any appreciable labilizing effect in contrast to the isoelectronic NH_2^- group. This is illustrated using the example of *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ and *cis*-$[Co(en)_2(OH)Cl]^+$ which both exhibit similar rate constants for the base-catalyzed substitution of Cl^- [30] [31]. Clearly, OH^- does not mimic the role of NH_2^-. The SCF MS-Xα calculations are in agreement with this experiment, since they show that in all the conjugate bases the HOMO represents the lone pair of the deprotonated amine ligand (*Fig. 2, Tables 3–5*). Replacement of NH_2^- by the isoelectronic OH^- or

H_2O ligands does not yield a particularly reactive species, since the p-orbital energy of oxygen is lower than that of nitrogen by ~ 1.4 eV and, therefore, the HOMO – LUMO gap will increase by ~ 1.4 eV. (Then, a metal d_π level may become the HOMO as in classical transition-metal complexes.) Doubtless, the enhanced reactivity of the conjugate base is due to the high-lying lone pair of the NH_2^- ligand and not to a simple charge effect.

According to the SCF MS-Xα calculations, the hexacoordinated intermediates are low-spin Co^{II} complexes, *viz. cis*-$[Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl]^+$, whereas the trigonal-bipyramidal intermediates exhibit a Co^{III} center in a triplet electronic ground state. The different electronic structures of these respective intermediates are corroborated by their dissimilar reactivities: the 'soft' low-spin Co^{II} center of hexacoordinated intermediates scavenges preferentially the 'soft' end of ambidentate ligands such as *e.g.* NCS^- [32–34] and furthermore, it does not react at all with the 'hard' F^- anion [35]. This behavior is contrasted by the shorter lived [2] pentacoordinated intermediates exhibiting a 'hard' Co^{III} center: the $[Co(NH_2CH_3)_4(NHCH_3)]^{2+}$ species captures preferentially the 'hard' N end of NCS^- [2]. Also, it should be noted that, under the same experimental conditions, the pentacoordinated intermediates $[Co(NH_2CH_3)_4(NHCH_3)]^{2+}$ and *mer*-[Co(dien – H)(dapo)]$^{2+}$ scavenge considerably more azide than the hexacoordinated intermediates *cis*-$[Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots X]^{n-1}$ [2–4] [6] [33].

Pentacoordinated intermediates are invoked quite frequently to be formed in the spontaneous or induced aquation of amine complexes of Co^{III}, although their existence *never* has been substantiated thus far; only the dissociative nature of the substitution process is established. According to the present calculations, pentacoordinated (and hexacoordinated) intermediates are very unlikely to exist in this case, since in the absence of a deprotonated amine ligand, stabilization of the electronic structure paralleling the dissociative activation cannot take place. A concerted mechanism (I_d) is likely to operate.

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