Aquation of the Chloro Pentaammine Complexes of Cobalt(III) and Chromium(III): Do the Almost Equal Activation Parameters Arise from a Common Mechanism?

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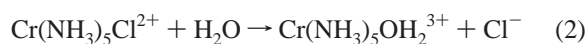Institut de chimie physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

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The activation parameters for the aquation of $Co(NH_3)_5Cl^{2+}$ and $Cr(NH_3)_5Cl^{2+}$ are almost equal, and the strongly negative volumes of activation, $\Delta V^{\ddagger}$ (-9.9 and -10.6 cm^3 mol^{-1} for Co and Cr, respectively), might at the first glance suggest a common associative mechanism for both complexes. Computations of the corresponding reaction coordinates indicate that, in agreement with Swaddle and co-workers' studies and as expected, a dissociative interchange mechanism (I_d) operates for cobalt(III), but an associative interchange one (I_a) for chromium(III). For these two asymmetric reactions, the bond lengths changes δ_{Co} and δ_{Cr} that are involved in the formation of the transition state and defined with respect to the fully concerted I pathway allow the attribution of the reaction mechanism. The signs of δ_{Co} and δ_{Cr}, being positive and negative, suggest a **d** and **a** activation for the above aquations.

Introduction

Pentaamine complexes of cobalt(III) are believed to undergo dissociatively activated ligand substitutions, because positive volumes of activation ($\Delta V^{\ddagger}$) have been measured for the replacement of neutral leaving groups by water in a variety of such compounds.[1−3] The relatively small positive activation volumes, being in the range of 0.3−6.3 cm^3 mol^{-1}, suggest the I_d mechanism.

It is striking, that the aquation of the chloropentaamminecobalt(III) ion, reaction 1, has a very negative volume of

$$Co(NH_3)_5Cl^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + Cl^- \quad (1)$$

$$Cr(NH_3)_5Cl^{2+} + H_2O \rightarrow Cr(NH_3)_5OH_2^{3+} + Cl^- \quad (2)$$

activation (-9.9 cm^3 mol^{-1} [4]) and especially that this value is very close to that of the corresponding reaction 2 of chromium-(III) (-10.6 cm^3 mol^{-1} [5]).
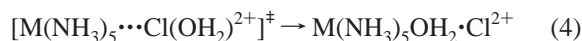
Ligand substitutions at the chromium(III) center are accepted to be associative on the basis of the negative $\Delta V^{\ddagger}$ for the substitution of neutral leaving groups in those pentaamine complexes.[6,7] The similarity of not only the volumes, but also the enthalpy and entropy of activation,[8,9] for the aquation of the chloro pentaammine complexes of cobalt(III) and chromium-(III) seems to be inconsistent with the mechanisms, I_d and I_a, respectively, derived from the water exchange. These data (the activation parameters) might suggest that the aquation of the

two chloro complexes proceeds via the same, associative, mechanism despite the disparate electronic structures of the two transition metal ions. The title question has already been treated by Swaddle and co-workers[4,5] more than 20 years ago. They attributed the I_d and I_a mechanisms to reactions 1 and 2, based on the linear dependence of $\Delta V^{\ddagger}$ on the reaction volume, ΔV°, and the positive and negative intercepts for the aquation of the respective $M(NH_3)_5X^{n+}$ complexes.

To get a deeper insight into these two aquations, the reaction coordinates of eqs 1 and 2 have been investigated with quantum chemical calculations, and it is shown how the structural changes occurring during the activation process can be related to the reaction mechanism. The present study confirms Swaddle and co-workers' conclusions[4,5] and gives detailed information on the bond making and breaking processes in the aquations 1 and 2.

Results and Discussion

Model. The previously used approach,[10−13] starting from the water adducts of the reactants, has been applied, and the geometries and energies of all species involved in eqs 3 and 4

$$M(NH_3)_5Cl \cdot OH_2^{2+} \rightarrow [M(NH_3)_5 \cdots Cl(OH_2)^{2+}]^{\ddagger} \quad (3)$$

$$[M(NH_3)_5 \cdots Cl(OH_2)^{2+}]^{\ddagger} \rightarrow M(NH_3)_5OH_2 \cdot Cl^{2+} \quad (4)$$

(M = Cr, Co) were computed. As a necessary improvement over the work on water exchange[10−13] where neutral ligands are involved, hydration effects had to be included for an adequate description of the substitution of the chloride anion by water. The zero point energy and electron correlation, however, were neglected as previously for the already discussed[10,12] reasons.

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(1) Lawrance, G. A. *Inorg. Chem.* **1982,** *21,* 3687.
(2) Curtis, N. J.; Lawrance, G. A. *Inorg. Chem.* **1986,** *25,* 1033.
(3) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958,** *80,* 2642.
(4) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972,** *50,* 2739.
(5) Guastalla, G.; Swaddle, T. W. *Can. J. Chem.* **1973,** *51,* 821.
(6) Curtis, N. J.; Lawrance, G. A.; van Eldik, R. *Inorg. Chem.* **1989,** *28,* 329.
(7) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972,** *94,* 8357.
(8) Chan, S. C. *J. Chem. Soc. A* **1967,** 291.
(9) Parris, M.; Wallace, W. J. *Can. J. Chem.* **1969,** *47,* 2257.

(10) Rotzinger, F. P. *J. Am. Chem. Soc.* **1996,** *118,* 6760.
(11) Rotzinger, F. P. *Chimia* **1997,** *51,* 97.
(12) Rotzinger, F. P. *J. Am. Chem. Soc.* **1997,** *119,* 5230.
(13) Kowall, Th.; Caravan, P.; Bourgeois, H.; Helm, L.; Rotzinger, F. P.; Merbach, A. E. *J. Am. Chem. Soc.* **1998,** *120,* 6569.

Table 1. Experimental and Computed Data for the Aquation of $Co(NH_3)_5Cl^{2+}$

param	$Co(NH_3)_5Cl\cdot OH_2^{2+}$		$[Co(NH_3)_5\cdots Cl(OH_2)^{2+}]^{\ddagger}$		$Co(NH_3)_5OH_2\cdot Cl^{2+}$
	exptl	calcd	exptl	calcd	calcd
$d(Co-N)$,[a] Å	1.973^b	2.03		1.99	2.02
$d(Co-Cl)$, Å	2.286^b	2.26		3.47	3.90
$d(Co-O)$, Å		4.03		2.86	1.95
$d(Co-X)_{av}$,[c] Å		3.15		3.16	2.93
$\sum d(Co-L)$, Å		16.45		16.30	15.98
$\sum d(Co-N)$, Å		10.16		9.97	10.12
$\Delta\sum d(Co-L)$, Å		0.00		-0.15	-0.47
$\Delta\sum d(Co-N)$, Å		0.00		-0.19	-0.04
$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$			-9.9^d		
E, hartrees		-515.790 238		-515.741 116	-515.778 223
ΔE or $\Delta E^{\ddagger}$, kJ/mol		0.00		129.0	31.5
$\Delta H^{\ddagger}/\Delta G^{\ddagger}$, kJ/mol			$93/106^e$		

[a] Average. [b] Reference 20. [c] Average of $d(Co-Cl)$ and $d(Co-O)$. [d] Reference 4. [e] Reference 8.

Table 2. Experimental and Computed Data for the Aquation of $Cr(NH_3)_5Cl^{2+}$

param	$Cr(NH_3)_5Cl\cdot OH_2^{2+}$		$[Cr(NH_3)_5\cdots Cl(OH_2)^{2+}]^{\ddagger}$		$Cr(NH_3)_5OH_2\cdot Cl^{2+}$
	exptl	calcd	exptl	calcd	calcd
$d(Cr-N)$,[a] Å	2.074^b	2.16		2.16	2.16
$d(Cr-Cl)$, Å	2.327^b	2.32		3.05	3.93
$d(Cr-O)$, Å		4.08		2.45	2.03
$d(Cr-X)_{av}$,[c] Å		3.20		2.75	2.98
$\sum d(Cr-L)$, Å		17.22		16.29	16.74
$\sum d(Cr-N)$, Å		10.82		10.79	10.78
$\Delta\sum d(Cr-L)$, Å		0.00		-0.93	-0.48
$\Delta\sum d(Cr-N)$, Å		0.00		-0.03	-0.04
$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$			-10.6^d		
E, hartrees		-457.570 366		-457.527 509	-457.557 480
ΔE or $\Delta E^{\ddagger}$, kJ/mol		0.00		112.5	33.8
$\Delta H^{\ddagger}/\Delta G^{\ddagger}$, kJ/mol	0.00		$93/102^e$		

[a] Average. [b] Reference 21. [c] Average of $d(Cr-Cl)$ and $d(Cr-O)$. [d] Reference 5. [e] Reference 9.

Structures and Energies. The geometries of the reactants, transition states and products of reactions 1 and 2 (or 3 and 4, respectively) were optimized at the Hartree−Fock level by taking into account solvation using the self-consistent reaction field model (SCRF).[14−16] The energies were then computed on the basis of the polarizable continuum model.[17−19] First, the transition states $[M(NH_3)_5\cdots Cl(OH_2)^{2+}]^{\ddagger}$ (M = Co, Cr) were computed as described previously.[10] Then, the reactants and products were obtained by the computation of the intrinsic reaction coordinate. Since no intermediate was found on the two reaction paths, both aquations follow an interchange mechanism. All these species exhibit C_s symmetry. Experimental and computed data for reactions 1 and 2 are summarized in Tables 1 and 2, respectively.

The M−N bond lengths are systematically too long due to the neglect of hydrogen bonding with the bulk solvent and dynamic electron correlation. All the limitations and approximations of this approach were discussed elsewhere[10,12] and are not repeated here. The $\sum d(M-L)$ and $\sum d(M-N)$ (M = Co, Cr) parameters represent the sum of all M−L or M−N bond lengths, respectively, whereas the corresponding $\Delta\sum d(M-L)$ and $\Delta\sum d(M-N)$ values are the respective differences between the transition state or the product and the reactant.

The calculated activation energies $\Delta E^{\ddagger}$ are higher than experimental $\Delta G^{\ddagger}$ values, because of the already mentioned limitations. The error is larger for Co (23 kJ/mol) than for Cr

(11 kJ/mol), but the energies are not critical for the discussion of the reaction mechanisms (Tables 1 and 2). The error in the M−N bond lengths might appear more severe for the attribution of the substitution mechanisms, but since it is systematic, it cancels out in the differences $\Delta\sum d(M-L)$ and $\Delta\sum d(M-N)$.

The significantly negative $\Delta\sum d(Co-N)$ value (Table 1) indicates that the activation process of reaction 1 is dissociative, since the electron density at the cobalt(III) center is reduced by the elongation of the Co−Cl bond (with the Co−O bond remaining long). This loss is compensated with a shortening of the Co−N bonds. For reaction 2, however, $\Delta\sum d(Cr-N)$ is close to zero (Table 2), because of the shorter Cr···Cl and Cr···O bonds in the transition state. The loss of electron density upon elongation of the Cr−Cl bond is smaller because of the concerted formation of the Cr···O bond; in the transition state, both Cr···Cl and Cr···O bonds are stronger than the corresponding Co···Cl and Co···O ones.

Geometry Changes along the Reaction Coordinates. The reactant and the product of reaction 1 are shown in Figures S1 and S2 (Supporting Information), and the corresponding transition state together with its imaginary mode is depicted in Figure 1. The structures of the corresponding chromium(III) complexes are similar with the difference that the Cr···Cl and Cr···O bond lengths in the transition state are shorter by approximately 0.4 Å (Tables 1 and 2). Plots of $\sum d(M-L)$ versus the reaction coordinate (Schemes 1 and 2), represented either as M−Cl or M−O bond lengths, show the difference between reactions 1 and 2. Since the latter are asymmetric with a net change of the reaction volume (or $\Delta\sum d(M-L)$), it is assumed that the volume change for a fully concerted reaction (I mechanism) occurs synchronously with the change of the M−Cl or M−O bond length. Therefore, the $\sum d(M-L)$ values of the reactants and

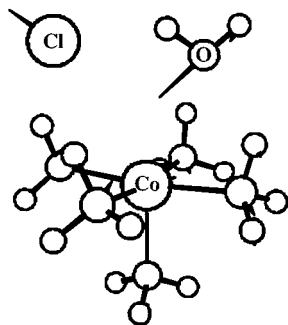(14) Kirkwood, J. G. *J. Chem. Phys.* **1934**, *2*, 351.
(15) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
(16) Szafran, M.; Karelson, M. M.; Katritzky, A. R.; Koput, J.; Zerner, M. C. *J. Comput. Chem.* **1993**, *14*, 371.
(17) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.
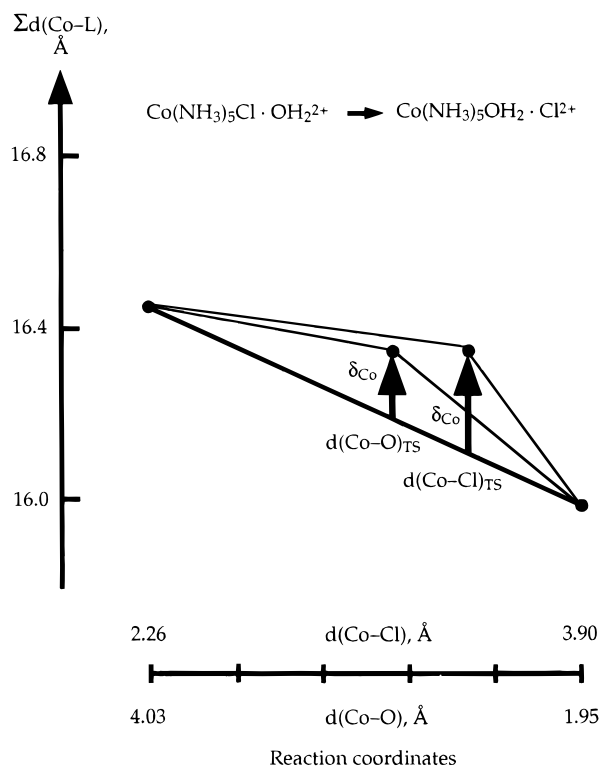(18) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.
(19) Tomasi, J.; Cammi, R. *J. Comput. Chem.* **1995**, *16*, 1449.

Figure 1. Perspective view and imaginary mode of the transition state $[Co(NH_3)_5\cdots Cl(OH_2)^{2+}]^{\ddagger}$.

Scheme 1

**Scheme 2**

products were connected with a straight line that represents $\sum d(M-L)$ as a function of the reaction coordinate for the hypothetical I mechanism. The transition state, characterized by $\sum d(M-L)$ and its corresponding M–Cl or M–O distance, $d(M-Cl)_{TS}$ or $d(M-O)_{TS}$, lies between. The important result is that, independent of the chosen reaction coordinate, $\sum d(Co-L)$ lies *above* the straight line (Scheme 1) for the aquation of $Co(NH_3)_5Cl^{2+}$, reaction 1, whereas for $Cr(NH_3)_5Cl^{2+}$, reaction 2, $\sum d(Cr-L)$ is *below* that line (Scheme 2). This means that, during the aquation of $Co(NH_3)_5Cl^{2+}$, the Co–L bond lengths do not diminish as much as expected for a fully concerted reaction (I mechanism), whereas, for $Cr(NH_3)_5Cl^{2+}$, the Cr–L bond lengths diminish more.

In other words, Scheme 1 shows that, in the transition state $[Co(NH_3)_5\cdots Cl(OH_2)^{2+}]^{\ddagger}$, the Co$\cdots$Cl and Co$\cdots$O bonds are longer than those expected for a fully concerted reaction. This is expressed by the positive δ_{Co} value. Therefore, bond breaking in the transition state prevails, and reaction 1 follows the I_d mechanism. In contrast, the transition state $[Cr(NH_3)_5\cdots Cl(OH_2)^{2+}]^{\ddagger}$ has Cr$\cdots$Cl and Cr$\cdots$O bonds shorter than expected for the fully concerted mechanism. In this case, δ_{Cr} is negative (Scheme 2), bond formation dominates, and reaction 2 therefore
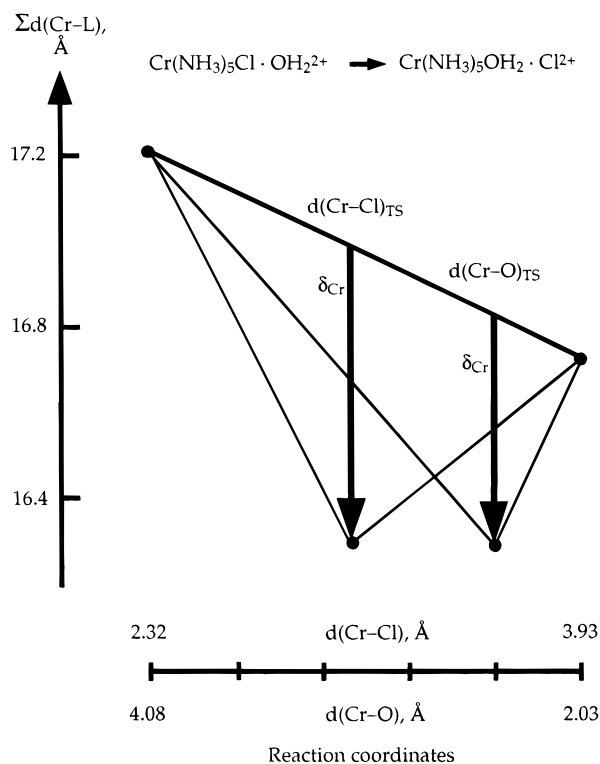
follows the I_a mechanism. Both reactions are concerted, because of the absence of any penta- or heptacoordinated intermediate along the reaction coordinate.

The present result is in perfect agreement with the reaction mechanisms attributed on the basis of the volumes of activation for the water exchange of the corresponding $M(NH_3)_5OH_2^{3+}$ ions[3,7] and the aquation[4,5] of $M(NH_3)_5X^{n+}$ complexes (M = Co, Cr; X = Cl⁻, Br⁻, NO₃⁻, SO₄²⁻).

The reaction volumes of 1 and 2 are both negative,[4,22] and so are the computed $\Delta\sum d(M-L)$ values (Tables 1 and 2). It should be noted, however, that the latter are based on the ion-pairs $M(NH_3)_5OH_2\cdot Cl^{2+}$ and not the dissociated products. Schemes 1 and 2 represent exclusively the substitution process that does not involve the dissociation of the ion-pairs $M(NH_3)_5$-$OH_2\cdot Cl^{2+}$. This latter step is irrelevant for the substitution mechanism, but of course, the experimental reaction volumes $(\Delta V°)$ include a component arising from the aquation and another one from the dissociation of the ion pair.

Computational Details

All the calculations were performed on HP 9000/735 and HP 9000/C200 computers using the GAMESS[23] program.

The basis sets of Stevens, Basch, Krauss, and Jasien[24] were used for cobalt and chromium, where the 1s, 2s, and 2p shells are represented by relativistic effective core potentials and the 3s, 3p, 4s, 4p shells have double-ζ and the 3d triple-ζ quality. For chloride, the basis set of Stevens, Basch, and Krauss,[25]

(20) Messmer, G. G.; Amma, E. L. *Acta Crystallogr.* **1968**, *B24*, 417.
(21) Hambley, T. W.; Lay, P. A. *Inorg. Chem.* **1986**, *2*, 5, 4553.
(22) Spiro, T. G.; Revesz, A.; Lee, J. *J. Am. Chem. Soc.* **1968**, *90*, 4000.
(23) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(24) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.
(25) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026.

supplemented with a 3d polarization function, was employed (α_{3d}(Cl) = 0.65 [26]). For N, O, and H 6-31G(d) basis sets[27,28] were used (α_{3d}(N) = 1.00,[26] α_{3d}(O) = 1.20 [26]).

For the SCRF calculations,[14−16] the cavity radius was taken as half of the value of the largest interatomic distance plus the two corresponding van der Waals radii. Once the geometry had converged, the cavity radius was redetermined, and if it differed by more than 0.01 Å from the previous value, the geometry optimization was repeated until the above criterion was fulfilled.

The atomic coordinates of all species involved in reactions 1 and 2 are given in Tables S1−S6 (Supporting Information).

Supporting Information Available: Tables listing the atomic coordinates of the reactant, transition state, and product of reactions 1 (Tables S1−S3) and 2 (Tables S4−S6) and figures (S1 and S2) depicting the reactant Co(NH$_3$)$_5$Cl·OH$_2$$^{2+}$ and product Co(NH$_3$)$_5$OH$_2$·Cl^{2+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(27) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(28) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.