2144 *Inorg. Chem.* **1987**, *26*, 2144-2149

Contribution from the Department of Inorganic Chemistry,
The University of Sydney, Sydney, NSW 2006, Australia

A Common Mechanism for the Spontaneous Aquations of Pentaaminecobalt(III) and Pentaaminechromium(III) Complexes. Ground-State Control Rather Than Activated-State Control of Kinetic Differences between Cobalt(III) and Chromium(III)

Peter A. Lay

Received November 7, 1986

The Cr–Cl bond in $[Cr(NH_3)_5Cl]Cl_2$ is significantly longer (0.03 Å) than that in $[Cr(NH_2CH_3)_5Cl]Cl_2$, which invalidates one of the original assumptions on which mechanistic differences between Cr(III) and Co(III) have been assigned. It is now apparent that the diminution in the rate of the spontaneous aquation of $[Cr(NH_2CH_3)_5Cl]^{2+}$, as compared to that of $[Cr(NH_3)_5Cl]^{2+}$, emanates from the stronger Cr–Cl bond in $[Cr(NH_2CH_3)_5Cl]^{2+}$, rather than the generally accepted notion of a steric retardation of an associative interchange mechanism. For the two cobalt complexes, the Co–Cl bond lengths are the same, within experimental error, and the rate constant is larger for $[Co(NH_2CH_3)_5Cl]^{2+}$ because of the greater relief of steric strain attained in a mechanism in which bond breaking substantially precedes bond making. In the Cr(III) complexes, this effect is more than counterbalanced by the stronger Cr–Cl bond in the ground state of the pentakis(methylamine) complex. The smaller acceleration of the rate of base hydrolysis in going from $[Cr(NH_3)_5Cl]^{2+}$ to $[Cr(NH_2CH_3)_5Cl]^{2+}$ (200-fold), as compared to that for the Co(III) analogues (10^4-fold), is probably due to a similar effect. The activation parameters for the spontaneous and base-catalyzed reactions have been reinterpreted and are entirely consistent with the assessments given above. The evidence suggests strongly that the degrees of bond breaking in the activated states are very similar in the substitution reactions of both Co(III) and Cr(III). On the balance of the experimental evidence currently available, they undergo substitution reactions by an I_d mechanism (in which bond breaking substantially precedes bond making) in their spontaneous reactions and an S_N1CB mechanism in their base-catalyzed aquations. Moreover, the neglect of the effects of Cr–Cl π-bonding makes spurious the previous steric and electronic arguments used to rationalize why Cr(III) complexes are more likely to undergo spontaneous substitution reactions by I_a mechanisms.

Introduction

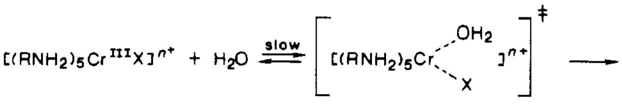
The classification of the mechanisms of substitution reactions at carbon centers into S_N1 (dissociative) and S_N2 (associative) processes has been well established for many years. However, the substitution reactions of the other elements have not been studied in as much detail and there still exists considerable controversy as to the mechanistic course of substitution reactions of many of the elements. The Co(III)–amine complexes have been the most studied systems of the transition elements, and it is now generally agreed that their spontaneous substitution reactions occur by mechanisms in which bond breaking substantially precedes bond making (eq 1),[1] while the base-catalyzed reactions occur via dissociative conjugate base mechanisms (S_N1CB) mechanisms (eq 2).[2-5]

$$[(RNH_2)_5Co^{III}X]^{n+} \xrightarrow{\text{slow}} [(RNH_2)_5Co^{3+}\cdots X^{(3-n)-}]^{\ddagger} \xrightarrow[H_2O]{\text{fast}} [(RNH_2)_5Co(OH_2)]^{3+} + X^{(3-n)-} \quad (1)$$

$$[(RNH_2)_5CoX]^{n+} + OH^- \rightleftarrows [(RNH_2)_4(RNH^-)CoX]^{(n-1)+} + H_2O$$

$$[(RNH_2)_4(RNH^-)CoX]^{(n-1)+} \xrightarrow{\text{slow}} [[(RNH_2)_4(RNH^-)Co]^{2+} + X^{(3-n)-}]^{\ddagger} \xrightarrow[H_2O]{\text{fast}} [(RNH_2)_5Co(OH)]^{2+} + X^{(3-n)-} \quad (2)$$

By contrast, Cr(III)–amine complexes are generally accepted to undergo spontaneous substitution reactions by mechanisms in which bond making precedes bond breaking (eq 3).[1-8] However,



$$[(RNH_2)_5Cr^{III}X]^{n+} + H_2O \xrightleftharpoons{\text{slow}} \left[[(RNH_2)_5Cr\begin{smallmatrix}\cdot\cdot OH_2 \\ \cdot\cdot X\end{smallmatrix}]^{n+} \right]^{\ddagger} \longrightarrow [(RNH_2)_5Cr(OH_2)]^{3+} + X^{(3-n)-}$$

(3)

Table I. M–Cl, M–N(trans), and M–N(av) Bond Distances (Å) in $[M(NH_3)_5Cl]Cl_2$, $[Cr(NH_2CH_3)_5Cl]Cl_2$, and $[Co(NH_2CH_3)_5Cl](NO_3)_2$[11-13]

	Co		Cr	
bond	NH_3	NH_2CH_3	NH_3	NH_2CH_3
M–Cl	2.286 (2)	2.283 (1)	2.327 (1)	2.299 (1)
M–N(trans)	1.964 (6)	1.980 (3)	2.070 (4)	2.103 (4)
M–N(av)	1.973	1.988	2.074	2.098

a recent study suggested that the mechanism of spontaneous substitution at Cr(III) differed little from that at Co(III) and that both undergo substitution reactions via mechanisms which are similar to those depicted in (1).[9] The purpose of the present study is to show that some of the original assumptions on which mechanistic differences between Co(III) and Cr(III) were purported to be established are incorrect. This is especially true for one of the most extensively studied systems from which the mechanistic behavior has been deduced for Cr(III) and Co(III) (i.e. $[M(NH_2R)_5Cl]^{2+}$.[2-10]). For spontaneous aquations, the rate constant is larger by a factor of 22 for $[Co(NH_2CH_3)_5Cl]^{2+}$ than it is for $[Co(NH_3)_5Cl]^{2+}$, but the reverse is the case for the Cr(III) complexes where the rate constant for $[Cr(NH_2CH_3)_5Cl]^{2+}$ is 33 times smaller than it is for $[Cr(NH_3)_5Cl]^{2+}$. These results and the interpretation of the activation parameters are often quoted as being proof of distinct mechanisms operating (i.e. I_d for Co(III) and I_a for Cr(III)).[2-9]

For base hydrolyses, with either metal ion, the rate constant is larger for the pentakis(methylamine) complex than it is for the respective pentaammine complex. This has been used to support a dissociative conjugate base mechanism (eq 2), in both instances.[2-9]

The underlying assumption for these mechanistic assignments has been that the Cr–Cl bond length is the same in both $[Cr(NH_2CH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_5Cl]^{2+}$. This seemed a reasonable assumption, since the Co–Cl bond lengths in $[Co(NH_3)_5Cl]Cl_2$[11]

---

[1] There have been several different definitions of an I_d mechanism,[2-5] but whenever it is used in this article, it implies a mechanism in which bond breaking is more important in the activated state than is bond making; i.e., bond breaking precedes bond making. Similarly, an I_a mechanism is used in the context of a mechanism in which there is a greater degree of bond making than bond breaking in the activated state.

[2] *Inorg. React. Mech.* **1971-1981**, *1-7*.

[3] Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *6*, 50-270.

[4] Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47-104.

[5] Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 1-94.

[6] Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 1790-1795.

[7] Parris, M.; Wallace, W. J. *Can. J. Chem.* **1969**, *47*, 2257-2262.

[8] Lawrance, G. A.; Schneider, K.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3922-3925.

[9] Curtis, N. J.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1986**, *25*, 484-488.

[10] A preliminary account of the present discussion has appeared: Lay, P. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1422-1423.

[11] Messmer, G. G.; Amma, E. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 417-422.

0020-1669/87/1326-2144$01.50/0

Table II. Rate Constants at 25 °C, Activation Parameters, and Molar Volumes for the Spontaneous Aquations of $[M(NH_2R)_5Cl]^{2+}$ [6-9,14-16]

	10^6k, s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta G^\ddagger$,[a] kJ mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}	$\Delta\beta^\ddagger$, cm^3 $kbar^{-1}$ mol^{-1}	V, cm^3 mol^{-1}
$[Co(NH_3)_5Cl]^{2+}$	1.72	93 (1)	−44 (3)	106	−9.9 (0.5)	−2.1 (0.2)	82.8
$[Co(NH_2CH_3)_5Cl]^{2+}$	39.6	95 (1.5)	−10 (4)	98	−2.3 (0.4)	~0	157.2
$[Cr(NH_3)_5Cl]^{2+}$	8.70	93 (0.5)	−29 (1.5)	102	−10.6 (0.3)	−1.0 (0.2)	87.5
$[Cr(NH_2CH_3)_5Cl]^{2+}$	0.261	110 (0.5)	−2 (1.5)	111	+0.5 (0.6)	~0	168.8

[a] At 25 °C, calculated from the published $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values.

Table III. Electronic Spectral Properties of $[M(NH_2R)_6]^{3+}$ and $[M(NH_2R)_5Cl]^{2+}$ (M = Co, Cr; R = H, CH_3)[18-23]

complex	d–d transitions,[a] 10^3 cm^{-1} σ_1	σ_2	Δ,[b] 10^3 cm^{-1}	B,[b,c] cm^{-1}
$[Co(NH_3)_5Cl]^{2+}$	18.66	27.25	19.38	652 (0.59)
$[Co(NH_3)_6]^{3+}$	21.05	29.41	22.04	612 (0.56)
$[Co(NH_2CH_3)_5Cl]^{2+}$	18.02	26.11	18.75	610 (0.55)
$[Co(NH_2CH_3)_6]^{3+}$	20.00	28.17	20.92	601 (0.55)
$[Cr(NH_3)_5Cl]^{2+}$	19.49	26.60	19.49	691 (0.75)
$[Cr(NH_3)_6]^{3+}$	21.55	28.50	21.55	657 (0.72)
$[Cr(NH_2CH_3)_5Cl]^{2+}$	19.08	25.91	19.08	660 (0.72)
$[Cr(NH_2CH_3)_6]^{3+}$	21.05	27.78	21.05	635 (0.69)

[a] $\sigma_1 = {}^1A_{1g} \rightarrow {}^1T_{1g}(Co)$, ${}^4A_{2g} \rightarrow {}^4T_{2g}(Cr)$. $\sigma_2 = {}^1A_{1g} \rightarrow {}^1T_{2g}(Co)$; ${}^4A_{2g} \rightarrow {}^4T_{1g}(Cr)$, for O_h symmetry. [b] Calculated from $\sigma_1 = \Delta - 4B + 86B^2/\Delta$ and $\sigma_2 = \Delta + 12B + 2B^2/\Delta$ (assuming $C = 4B$) for Co(III) and $\sigma_1 = \Delta$ and $\sigma_2 = \Delta - 12B - y$, ($y = 36B^2/(\Delta - 9B + y)$) for Cr(III). [c] Values of β calculated by using the free ion values of 1100 cm^{-1} for Co(III) and 918 cm^{-1} for Cr(III)[23] are in parentheses.

and $[Co(NH_2CH_3)_5Cl](NO_3)_2$[12] are the same, within experimental error, despite the steric crowding in the latter complex.[12] It was somewhat surprising that the X-ray crystal structure of $[Cr(NH_3)_5Cl]Cl_2$ was not known until recently,[13] and even more surprising is the observation that the Cr–Cl bond is significantly longer (0.03 Å) than that observed in the structure of the more sterically crowded complex in $[Cr(NH_2CH_3)_5Cl]Cl_2$.[12] Indeed, the Cr–Cl bond length in $[Cr(NH_2CH_3)_5Cl]Cl_2$ is more comparable to the two Co–Cl bond lengths than to the Cr–Cl bond length in $[Cr(NH_3)_5Cl]Cl_2$.[13] In light of these completely unexpected bond length results, the mechanisms deduced from the kinetic data needed to be reevaluated. This is the subject of the ensuing discussions.

Discussion

Variations in the Ground-State Properties of the $[M(NH_2R)_5Cl]^{2+}$ Ions. Table I summarizes crystallographic bond length data for $[M(NH_2R)_5Cl]Cl_2$ (M = Co, R = H;[11] M = Cr, R = H,[13] CH_3[12]) and for $[Co(NH_2CH_3)_5Cl](NO_3)_2$,[12] while Table II contains rate constants and activation parameters for the acid aquations of the $[M(NH_2R)_5Cl]^{2+}$ ions.[6-9,14-16]

From Table I, the M–N(av) bond lengths are ~0.1 Å greater for the Cr(III) complexes as compared to the Co(III) complexes, which relieves the steric crowding in the ground state of the pentakis(methylamine)chromium(III) complex more than in the pentakis(methylamine)cobalt(III) complex.[12] For the cobalt complexes, the Co–Cl bond lengths are the same within experimental error. The strong implication is that the strength of the Co–Cl bonds in the two ground states are comparable. The M–N(av) bond length is slightly longer (0.015 Å) in the pentakis(methylamine)cobalt(III) complex than in the pentaammine complex, although the experimental errors are such that this difference cannot be stated with confidence.[12] By contrast, the Cr–Cl bond length of 2.299 (1) Å in $[Cr(NH_2CH_3)_5Cl]Cl_2$ is 0.028 Å shorter than the value of 2.327 (1) Å observed in $[Cr(NH_3)_5Cl]Cl_2$.[12,13] Thus, the strength of the Cr–Cl bond in the ground state is expected to be considerably greater for the pentakis(methylamine) complex as opposed to the pentaammine complex. The experimental errors in the Cr–N(av) bond lengths are larger than in the Cr–Cl bond lengths, but there appears to be a concomitant lengthening of the M–N(av) bond length by 0.024 Å in going from $[Cr(NH_3)_5Cl]Cl_2$ to $[Cr(NH_2CH_3)_5Cl]Cl_2$. In particular, the Cr–N(trans) bond elongates significantly (0.033 Å) in going from the pentaammine complex to the pentakis(methylamine) complex.[12,13] The manner of the distortions in the metal–ligand bond lengths of $[Cr(NH_2CH_3)_5Cl]^{2+}$ from those present in the structure of $[Cr(NH_3)_5Cl]Cl_2$ was unexpected for a sterically hindered ion. Even more surprising was the observation that the average Cl–Cr–N(cis) bond angle is 90.9°,[12] which is slightly larger than the 90.5° observed in $[Cr(NH_3)_5Cl]Cl_2$.[13] Normally, it would be expected that this angle would be less than 90°, in order to relieve the steric clashes between the methylamine ligands. Indeed, in the cobalt analogues, the average Cl–Co–N(cis) bond angle was reduced from 89.4° in the pentaammine complex to 88.5° in the pentakis(methylamine) complex.[11-13]

Recently, it was shown that within the isomorphous series for $[M(NH_3)_5Cl]Cl_2$, M = Cr, Ru, Os, Co, Rh, and Ir, the ratio of the M–Cl to M–N(av) bond lengths is significantly smaller for the d^3 and d^5 ions, as opposed to the d^6 ions. This is consistent with the general expectations of the strengths of the M–Cl π-bonding.[13] Additionally, the average Cl–M–N(cis) bond angles are ≳1° larger for the d^3 and d^5 ions than those found for the d^6 ions. This is most probably due to the greater spatial requirements of multiple bonding within the M–Cl bond.[13] These considerations allow the rationalization of the different ways in which the two pentakis(methylamine) complexes relieve steric strain. In $[Co(NH_2CH_3)_5Cl](NO_3)_2$, the steric clashes are reduced by alternating the M–N bonds between long and short bonds (1.979–1.998 Å) and closing the average Cl–Co–N(cis) bond angle to 88.5°. While this would result in more strain on the Co–Cl bond in the pentakis(methylamine) complex as compared to the pentaammine complex, the slight lengthening of the Co–N(trans) bond from 1.964 (6) Å in $[Co(NH_3)_5Cl]Cl_2$ to 1.980 (3) Å in $[Co(NH_2CH_3)_5Cl](NO_3)_2$ appears to counterbalance the increased strain. This enables the Co–Cl bond length to remain essentially the same in the two complexes. However, the spatial requirements of the Cr–Cl multiple bond (Co–Cl π-bonding is expected to be weak in comparison[13]) would inhibit a closing of the Cl–Cr–N(cis) bond angle, and it appears to be more energetically favorable to lengthen the Cr–N bonds further, in order to relieve steric clashes. In particular, the Cr–N(trans) bond elongates by 0.033 Å; this in turn allows the Cr–Cl bond to shorten and increase its π-bonding, thus increasing the average Cl–Cr–N(cis) bond angle. It also allows the cis methylamine ligands to bend away from the Cr–Cl multiple bond without too much increase in strain energy. These options are not as favorable for Co(III) because of its smaller radius and smaller tendency to form Co–Cl π-bonds.[13] A further point is that the differences in the ground states of these complexes cannot be explained simply by steric factors, as molecular mechanics calculations lead to preferred geometries different from those observed in the methylamine structures.[17]

From the above results and analyses, it is clear that it would be more difficult to stretch the Cr–Cl bond to a given distance in $[Cr(NH_2CH_3)_5Cl]^{2+}$ than in $[Cr(NH_3)_5Cl]^{2+}$, if the same structures persisted in aqueous media. Evidence which supports the expectations that the π-bonding observed in the solid state

---

(12) Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932–1938.
(13) Hambley, T. W.; Lay, P. A. *Inorg. Chem.* **1986**, *25*, 4553–4558.
(14) Chan, S. C. *J. Chem. Soc. A* **1967**, 291–295.
(15) Jones, W. E.; Carey, L. R.; Swaddle, T. W. *Can. J. Chem.* **1972**, *50*, 2739–2746.
(16) Guastalla, G.; Swaddle, T. W. *Can. J. Chem.* **1973**, *51*, 821–827.
(17) Hambley, T. W., unpublished results.

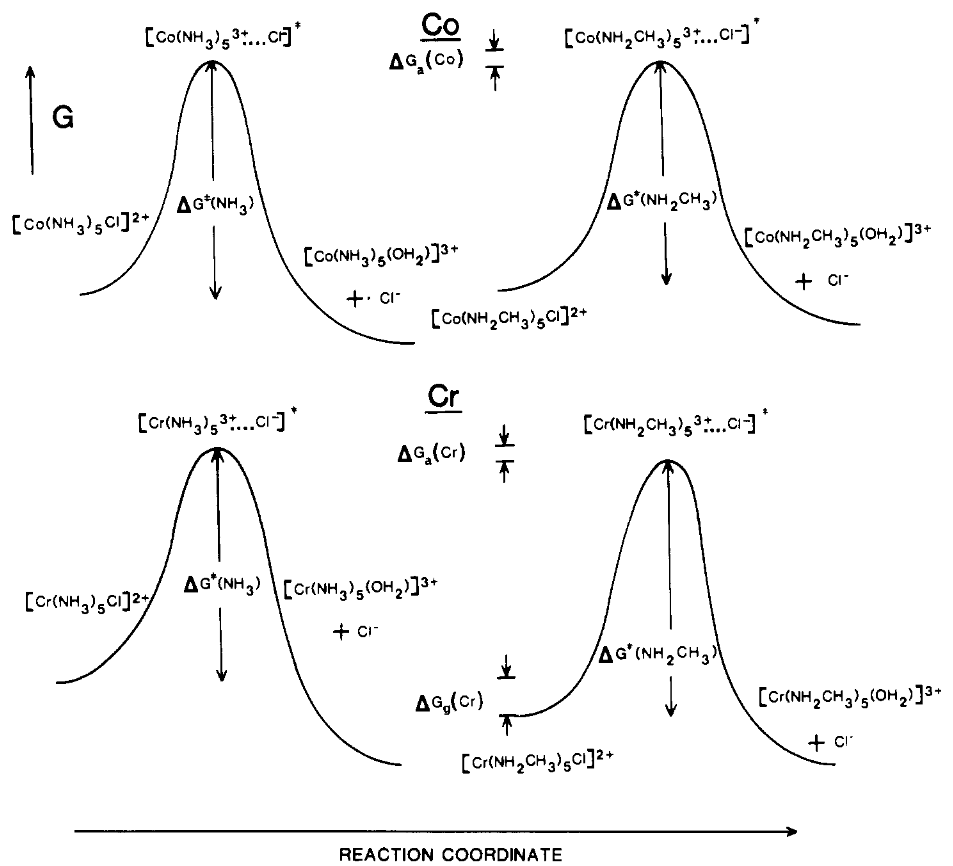


Figure 1. Plots of free energy vs. the reaction coordinates in the spontaneous aquations of $[M(NH_2R)_5Cl]^{2+}$.

of the Cr(III) complexes carries over into solution is to be found in the energies of the spin-allowed d–d transitions in the electronic absorption spectra of the Co(III) and Cr(III) complexes (Table III).[18-21] In the calculation of the values of the ligand field parameters, Δ, and the Racah B parameters (nephelauxetic ratio β), the second-order effects have been taken into account.[22,23] The average values of Δ and B for the pentaamine chloro complexes have been estimated by using the equations appropriate to octahedral symmetry. While this will not give an accurate measure of the overall ligand field, the trends in Δ and β are useful for comparative purposes.

The first point worthy of note is that the difference in Δ between $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_2CH_3)_6]^{3+}$ is smaller than that between $[Co(NH_3)_6]^{3+}$ and $[Co(NH_2CH_3)_6]^{3+}$. This is consistent with the greater steric crowding expected in $[Co(NH_2CH_3)_6]^{3+}$ as compared to $[Cr(NH_2CH_3)_6]^{3+}$ (due to the smaller ionic radius of the former metal ion).[12] The second point to note is that the difference in Δ between $[M(NH_3)_5Cl]^{2+}$ and $[M(NH_3)_6]^{3+}$ is smaller in Cr(III) than Co(III). This is consistent with the stronger π-bonding of the chloro ligand to Cr(III) as opposed to Co(III),[13] as this will increase the value of Δ for the Cr(III) complexes with respect to the Co(III) complexes. A third feature is that the difference between Cr and Co in their Δ values for $[M(NH_3)_5Cl]^{2+}$ and $[M(NH_2CH_3)_5Cl]^{2+}$ is smaller in the pentakis(methylamine) complexes as compared to the pentaammine complexes. This supports the stronger Cr–Cl bond observed in $[Cr(NH_2CH_3)_5Cl]Cl_2$ carrying over into solution.

Implications of the Variations in the Ground-State Energies of the M–Cl Bonds on the Kinetics and Mechanisms of Spontaneous Aquations. Since the experimental data suggests that the ground-state properties shown to exist in the solid state also persist in solution, the observed differences in the kinetics of the spontaneous aquations can be accounted for readily (without the need to invoke a change in mechanism). Quite simply, because the Cr–Cl bond in $[Cr(NH_2CH_3)_5Cl]^{2+}$ is significantly shorter than the corresponding bond in $[Cr(NH_3)_5Cl]^{2+}$, it requires more energy to stretch the bond to a given distance, and hence, the rate of aquation is retarded in $[Cr(NH_2CH_3)_5Cl]^{2+}$ as compared to $[Cr(NH_3)_5Cl]^{2+}$ for a mechanism in which bond breaking substantially precedes bond making. Apparently, the extra free energy of activation required for stretching the Cr–Cl bond in $[Cr(NH_2CH_3)_5Cl]^{2+}$ is sufficient to more than counterbalance the decrease in the free energy of activation due to relief of steric clashes in the activated state. Since only the latter effect operates for the cobalt complexes, the rate is accelerated in the $[Co(NH_2CH_3)_5Cl]^{2+}$ ion as compared to the $[Co(NH_3)_5Cl]^{2+}$ ion. Thus, the differences in kinetic behavior are readily explained within the framework of an I_d mechanism.

This explanation is also supported by a detailed analysis of the published activation parameters, which will be discussed with the aid of the reaction coordinate diagrams given in Figure 1 (for all four complexes). In constructing these diagrams, it has been assumed that the degree of dissociation of the M–Cl bond in the activated state is the same in all instances, which will be shown to be compatible with the activation parameters. The values of ΔG^* at 25 °C collected in Table II have been calculated from the published values of ΔH^* and ΔS^*. Because the two Co–Cl bond lengths are about the same in the ground state, the difference, $\Delta(\Delta G^*(Co)) = [\Delta G^*(NH_2CH_3) - \Delta G^*(NH_3)]$, for Co(III) is due mainly to the difference in the free energies of the activated states, $\Delta G_a(Co)$, while the difference between the ground states, $\Delta G_g(Co)$ is approximately 0. From Table II, $\Delta G_a(Co) \sim 8$ kJ mol^{-1} and the major part of this term is an entropy factor. The activation enthalpy is slightly higher for $[Co(NH_2CH_3)_5Cl]^{2+}$ than for $[Co(NH_3)_5Cl]^{2+}$, which is probably due to the more negative contributions of solvation enthalpy to ΔH^* for the ammine complex. This is discussed in more detail later in this section. Thus, not only is the Co–Cl bond the same length in the ground state

---

(18) Swaddle, T. W. *Can. J. Chem.* **1977**, *55*, 3166–3171.
(19) Mitzner, R.; Depkat, W.; Blankenburg, P. *Z. Chem.* **1970**, *10*, 34–35.
(20) Wong, C. F. C.; Kirk, A. D. *Can. J. Chem.* **1975**, *53*, 419–426.
(21) Parris, M.; Feiner, N. F. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 337–338.
(22) Jørgensen, C. K. *Modern Aspects of Ligand Field Theory*; North-Holland: Amsterdam, 1971.
(23) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: London, 1962.

of both complexes but also the stretching of the bond in the activated state appears to be comparable ($\Delta H^\ddagger$ approximately constant).

If it is assumed that the lowering in free energy of the activated state of $[Cr(NH_2CH_3)_5Cl]^{2+}$ is comparable to that for the cobalt analogue for an I_d mechanism, then $\Delta G_a(Cr) \sim \Delta G_a(Co)$. With this assumption, the differences in the free energy of the Cr–Cl bonds in the ground state, $\Delta G_g(Cr)$, is calculated to be −17 kJ mol^{-1}. This is exactly the observed difference in the enthalpy of activation of the aquation of the two chromium complexes. Thus, the retardation in the rate of spontaneous aquation of $[Cr(NH_2CH_3)_5Cl]^{2+}$, as compared to that of $[Cr(NH_3)_5Cl]^{2+}$, is merely a reflection of the difference in energy required to stretch the two different Cr–Cl bonds from their ground-state values to a similar distance in the activated state (near the dissociative limit). Moreover, if both the chromium and cobalt complexes react via a common mechanism, which involves a similar degree of bond breaking in the activated state, the differences in the entropy of activation between the pentaammine and pentakis(methylamine) complexes should be very nearly the same for both cobalt and chromium. Indeed, the differences are ~30 J K^{-1} mol^{-1}, for both metal ions, which would be difficult to reconcile if the mechanisms were different. All these results suggest that the mechanisms for both Cr(III) and Co(III) have a similar degree of bond breaking.

The more negative values of $\Delta S^\ddagger$ observed for the Co(III) complexes compared to their Cr(III) analogues are probably a reflection of the differences in the complex/solvent interactions. The Cr(III) complexes have larger radii than the Co(III) complexes, which will have the effect of increasing both the Born (dielectric continuum) and the specific hydrogen-bonding solvations of the Co(III) complexes with respect to those of their Cr(III) analogues.[7,13,18] Therefore, the $\Delta S^\ddagger$ component due to the differences in the solvation of the amine ligands in the ground and activated states of the complexes will be more negative for Co(III) than for Cr(III). By contrast, the chloro ligand will be more strongly solvated in the Cr(III) complexes due to the longer Cr–Cl bonds.[13] Thus, the contribution of the solvation of the chloro ligands to the entropy change during the stretching of a M–Cl bond to the dissociative limit will also be more negative for Co(III). The additive effects of these two components will result in $\Delta S^\ddagger$ being more negative for Co(III) as compared to Cr(III) for an I_d mechanism. Again, this is exactly what is observed, so that the $\Delta S^\ddagger$ values do not necessarily support a change in the mechanism.

Further, the difference between $\Delta S^\ddagger$ values for the pentaammine complexes should be somewhat larger than that between the pentakis(methylamine) complexes for an I_d mechanism. This is because the methylamine complexes will be less strongly solvated than the ammine complexes,[7,13,18] thus decreasing the solvation contribution to $\Delta S^\ddagger$. In addition, the Cr–Cl bond length in $[Cr(NH_2CH_3)_5Cl]^{2+}$ is closer to a Co–Cl bond length than the Cr–Cl bond length observed in $[Cr(NH_3)_5Cl]^{2+}$. This will lead to a smaller difference in $\Delta S^\ddagger$ due to the differences in solvation of the chloro ligand in the ground and excited states of the methylamine complexes, as opposed to the ammine complexes. Again, the experimental observations are consistent with these arguments based on an I_d mechanism, since $\delta(\Delta S^\ddagger)$ is 8 J K^{-1} mol^{-1} for the pentakis(methylamine) complexes and 15 J K^{-1} mol^{-1} for the pentaammine complexes.

The invoking of a common mechanism also accommodates the activation volume data;[8] i.e., $\Delta V^\ddagger$ increases by 7.6 cm^3 mol^{-1} in going from $[Co(NH_3)_5Cl]^{2+}$ to $[Co(NH_2CH_3)_5Cl]^{2+}$, while the corresponding increase in the Cr(III) complexes is 11.1 cm^3 mol^{-1}. The 7.6 cm^3 mol^{-1} difference in the cobalt complexes is most likely due to the same factors that give rise to the increase in the entropy.[24] If a common mechanism were to apply, the additional 3.5 cm^3 mol^{-1} observed for the chromium complexes is consistent with the shorter Cr–Cl bond length in $[Cr(NH_2CH_3)_5Cl]^{2+}$ as opposed to $[Cr(NH_3)_5Cl]^{2+}$, (i.e. the Cr–Cl bond in $[Cr(NH_2CH_3)_5Cl]^{2+}$ has to stretch more than that in $[Cr(NH_3)_5Cl]^{2+}$, hence the more positive value of $\Delta V^\ddagger$). Apart from the rationalization above, the observation that $\Delta V^\ddagger$ is the same, within experimental error, for both of the pentaammine complexes suggests strongly that a common mechanism applies.

Finally, the values for the compressibility coefficients of activation, $\Delta\beta^\ddagger$, are the same in the two pentakis(methylamine) complexes, which mitigates against a change in mechanism. The more negative value of $\Delta\beta^\ddagger$ observed for $[Co(NH_3)_5Cl]^{2+}$ as compared to that for $[Cr(NH_3)_5Cl]^{2+}$ is probably due to the greater contributions of solvation to the activation parameters for the Co(III) complex (as discussed previously for the entropy).

Steric and Electronic Factors. The ligand field contributions to the d^3 and d^6 electronic configurations destabilize both five-coordinate and seven-coordinate intermediates with respect to their six-coordinate ground states, which accounts for their inertness to substitution reactions.[25] Moreover, the destabilization of the two lowest energy intermediates is virtually the same for either an octahedral-wedge (seven-coordinate) or a square-pyramidal (five-coordinate) intermediate, for either metal ion. The strong implication is that, other factors being equal, both metal ions should undergo substitution reactions by the same mechanism. However, electronic and steric factors have been invoked to rationalize the previous proposals that the mechanisms are different for Cr(III) and Co(III). Thus, for Co(III), it has been deduced from the stereochemical course of reactions that steric factors favor an I_d mechanism to such an extent that the five-coordinate intermediate distorts toward a higher energy trigonal-bipyramidal geometry during the substitution reactions.[26,27] It has been argued often that the larger Cr(III) ion would enable a seven-coordinate intermediate to be more sterically accessible than that for Co(III) and that the d^3 electronic configuration would assist an associative mechanism by enabling an incoming nucleophile to form a bond via an empty d orbital.[25,28] This would explain why the Cr(III) substitution reactions are more stereoretentive, but both of these arguments are based on false assumptions. First, the average Cl–M–N(cis) bond is greater than 90° for Cr(III) but less than 90° for Co(III), which indicates that repulsion by the Cr–Cl multiple bond would inhibit nucleophilic attack at a cis position to a greater extent for Cr(III) than for Co(III). Second, the d orbitals cis to the Cr–Cl bond are already involved with π-bonding, which will inhibit cis bond formation with an incoming nucleophile. Thus, contrary to popular opinion, cis attack of a nucleophile to a $[Cr^{III}(NH_2R)_5X]^{n+}$ complex, where X is a π-bonding ligand, will not be enhanced as compared to that to a Co(III) complex. Since the stereochemical results on a range of Cr(III) complexes show that trans attack of a nucleophile does not take place,[26,27] then the electronic and steric arguments are consistent with an I_d mechanism operating for both Cr(III) and Co(III). The probable differences in the stereochemical courses of the substitution reactions of the two metal ions,[26,27] is that the intermediate is more distorted toward a trigonal-bipyramidal shape for the Co(III) complexes, than for the larger Cr(III) complexes. The different geometries of the activated states also impinges on the arguments that, on ligand field grounds, $\Delta H^\ddagger$ should be ~25 kJ mol^{-1} less for Cr(III) than for Co(III).[25] The distortion of the activated state of Co(III) toward a trigonal-bipyramidal geometry, which is less energetically favored[25] than the square pyramid preferred by Cr(III), will reduce this difference. The value of $\delta(\Delta H^\ddagger)$ is reduced further by the more negative solvent contributions to $\Delta H^\ddagger$ for Co(III) as compared to Cr(III). These solvation effects arise from the hydrogen-bonding and Born enthalpy terms being more important in the activated states than the ground states, because of the separation of the charge centers in an I_d mechanism.[25] They are more important for Co(III) than for Cr(III) because of the smaller ionic radius of Co(III). The greater contributions of π-bonding to Cr(III) as compared to Co(III)[13]

---

(24) Lawrance, G. A.; Stranks, D. R. *Acc. Chem. Res.* **1979**, *12*, 403–409.

(25) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions: A Study of Metal Ions in Solution*, 2nd ed.; Wiley: New York, 1967; Chapter 3.

(26) Reference 25; Chapter 4.

(27) Jackson, W. G.; Sargeson, A. M. *Org. Chem. (N.Y.)* **1980**, *42*, 273–378.

(28) Swaddle, T. W. *Adv. Inorg. Bioinorg. Chem.* **1983**, *2*, 95–138.

Table IV. Rate Constants at 25 °C and Activation Parameters for the Base Hydrolysis of $[M(NH_2R)_5Cl]^{2+}$

	k, s^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta G^\ddagger$, kJ mol^{-1}	ref
$[Co(NH_3)_5Cl]^{2+}$	0.24	118	74	96	36
$[Co(NH_2CH_3)_5Cl]^{2+}$	1.8×10^3	78	72	57	35
$[Cr(NH_3)_5Cl]^{2+}$	1.9×10^{-3}	112	77	89	7
	1.8×10^{-3}	110	54	94	38
$[Cr(NH_2CH_3)_5Cl]^{2+}$	0.43	106	103	75	7

would tend to negate the remaining difference (for an I_d mechanism), because it makes Cl^- a stronger field ligand for Cr(III) as compared to Co(III).[29] Thus, the observation that $\Delta H^\ddagger$ is the same for both Cr(III) and Co(III) in the aquation of $[M(NH_3)_5Cl]^{2+}$ is fortuitous and is not expected to be the norm.

Comparisons with Other Systems. Detailed studies on the $[M(NH_2R)_5(OSO_2CF_3)]^{2+}$ complexes,[9,30] have led to the conclusion that bond breaking precedes bond making by a substantial margin in the spontaneous aquations of both Cr(III) and Co(III),[9] which supports the conclusions drawn from the present work. This is reinforced by the observation that the rate constants for substitution reactions of Cr(III) are independent of the entering group, even when a good nucleophile such as RS^- is used.[9]

The differences in $\Delta V^\ddagger$ for aqua exchange in $[Co(NH_3)_5(OH_2)]^{3+}$ (+1.2 cm^3 mol^{-1})[31] and $[Cr(NH_3)_5(OH_2)]^{3+}$ (−5.8 cm^3 mol^{-1})[32] have been quoted as proof of an I_d mechanism operating for Co(III) and an I_a mechanism operating for Cr(III). However, the smaller ionic radius of Co(III) results in the aqua ligand being more compressed in $[Co(NH_3)_5(OH_2)]^{3+}$ than when it is coordinated to Cr(III). This would lead to a more positive volume of activation for Co(III) than for Cr(IIII) in order to stretch the M–O bond to the same distance in the activated states. Second, the Co(III) aqua ligands will be more polarized than those coordinated to Cr(III)[13] and hence will form stronger hydrogen bonds to solvent molecules in the first hydration sphere. Thus, the decrease in electrostriction of hydrogen-bonding water molecules will be greater for Co(III) than for Cr(III), again leading to a more positive value of $\Delta V^\ddagger$ for Co(III). The compressibility coefficients of activation for both complexes are essentially zero, which is also a strong indication that the mechanism does not change. These factors combined indicate that the activated states for Cr(III) and Co(III) are more similar than most people have assumed and that there is more bond breaking than bond making in the activated states of the water-exchange reactions of both complexes.

The lower value of $\Delta H^\ddagger$ for Cr(III) as compared to that for Co(III) ($\delta(\Delta H^\ddagger)$ = 14 kJ mol^{-1}) for water exchange in $[M(NH_3)_5(OH_2)]^{3+}$[31,32] is probably a reflection of both crystal field effects and the less important contributions of solvation and π-bonding terms than is the case for the aquation of the $[M(NH_3)_5Cl]^{2+}$ complexes. For an I_d mechanism (near the dissociative limit with a similar stretching of the M–O bond in the activated state), it is expected that $\Delta H^\ddagger$ should be approximately 40 kJ mol^{-1} less for Cr(III) as opposed to that for Co(III), on ligand field grounds.[25] While the effect of the preferred geometry of the activated state plus the effects of π-bonding and solvation will tend to decrease $\Delta H^\ddagger$ for Co(III) as compared to that for Cr(III), this is more than compensated for by the increase in the ligand field contribution. Thus, the observation that $\Delta H^\ddagger$ is approximately equal in the aquations of $[M(NH_3)_5Cl]^{2+}$ but is smaller for the water-exchange reaction of $[Cr(NH_3)_5(OH_2)]^{3+}$ as compared to the reaction of the Co(III) analogue is compatible with a uniform I_d mechanism.

That the major difference between the substitution rates of $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_2CH_3)_5Cl]^{2+}$ is due to the differences in the strength of solvation of the amine ligands between the ground and excited states is supported by the comparisons of the rate constants at 25 °C for water exchange in $[Co(NH_2R)_5(OH_2)]^{3+}$ (5.9×10^{-5} s^{-1}, R = H;[31] 1.1×10^{-4} s^{-1}, R = CH_3[33]). There is only a 2-fold increase in going to the more sterically hindered complex in these reactions, where the charge of the complex remains the same in both the activated and ground states. Therefore, the differences in solvation of the ground and excited states will be due mainly to the differences in solvation of the leaving group. Since this will be about the same for both complexes, it is to be expected that the rate constants will be approximately the same. This also supports the analysis that the differences in $\Delta S^\ddagger$ for the chloro complexes are due to solvation effects, for a given metal ion.

When the neutral leaving group is more bulky than water, the aquation rate constants are much larger for $[Co(NH_2CH_3)_5L]^{3+}$ than $[Co(NH_3)_5L]^{3+}$.[34] However, for a given leaving group, most of the difference lies in a more positive value of $\Delta S^\ddagger$ for $[Co(NH_2CH_3)_5L]^{3+}$ ($\Delta H^\ddagger$ approximately constant). This more positive value of $\Delta S^\ddagger$ is most probably due to a greater relief of steric rigidity in going from the ground to activated states of the $[Co(NH_2CH_3)_5L]^{3+}$ complexes as compared to the $[Co(NH_3)_5L]^{3+}$ complexes but does not appear to be important for a small ligand such as water. These analyses indicate that the ground-state bond lengths of the leaving groups do not differ by a great deal in the pentaammine and pentakis(methylamine) complexes.

The same arguments may not be valid for the substitution reactions of $[M(NH_2R)_6]^{3+}$, where none of the ligands are involved in π-bonding. In these instances, the much different degrees of inertness may be due to a changeover in the mechanism of the substitution reactions with electronic configurations (i.e. d^3 and d^5 configurations are likely to have a higher degree of associative character in their substitution reactions).

Base-Catalyzed Hydrolyses. Rate constants at 25 °C and activation parameters for the base-catalyzed hydrolyses of $[M(NH_2R)_5Cl]^{2+}$ are contained in Table IV.[7,25,35–38] The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the Co(III) complexes are of limited accuracy, but the calculated values of $\Delta G^\ddagger$ at 25 °C are more reliable due to the compensation of errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$.[4]

There is considerable evidence that the base-catalyzed substitution reactions of Co(III)- and Cr(III)-amine complexes both follow the limiting case of a dissociative conjugate base mechanism.[5,7,9,39] Even the competition ratios for capture of azide as opposed to water by the proposed five-coordinate intermediates are identical in the base hydrolyses of $[M(NH_3)_5(OSO_2CF_3)]^{2+}$.[9] Despite this, one result which has not been adequately rationalized is that the base-hydrolysis of $[Co(NH_2CH_3)_5Cl]^{2+}$ has a rate constant which is 8000–15000 times greater than that for $[Co(NH_3)_5Cl]^{2+}$,[6] while the corresponding difference is only 230 for

---

(29) Although π-bonding is often stated as reducing the ligand field for Cr(III), (e.g.: Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1983; pp 295–297), this does not take into account the synergistic effects that will increase σ-bonding concomitantly. Moreover, such arguments normally deal only with the effects of π-bonding on the e_g and t_{2g} subset of d orbitals and not the entire ligand field. It is axiomatic that when the strength of the metal–ligand bond increases, the total ligand field must also increase.

(30) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2940–2947.

(31) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642–2646.

(32) Swaddle, T. W.; Stranks, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 8357–8360.

(33) Shaver, A. G.; Parris, M. *Can. J. Chem.* **1973**, *51*, 1392–1396.

(34) Curtis, N. J.; Lawrance, G. A. *Inorg. Chem.* **1986**, *25*, 1033–1037.

(35) Mitzner, R.; Depkat, W. *Z. Phys. Chem.* (*Leipzig*) **1973**, *254*, 189–195.

(36) Chan, S. C.; Hui, K. Y.; Miller, J.; Tsang, W. S. *J. Chem. Soc.* **1965**, 3207–3217.

(37) Adamson, A. W.; Basolo, F. *Acta Chem. Scand.* **1955**, *9*, 1261–1274.

(38) Levine, M. A.; Jones, T. P.; Harris, W. E.; Wallace, W. J. *J. Am. Chem. Soc.* **1961**, *83*, 2453–2457.

(39) Comba, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 51–52.

the Cr(III) analogues (Table IV). However, these differences are explained readily by the extra contribution to ΔH^* of 17 kJ mol^{-1}, which is required to break the shorter Cr–Cl bond of the pentakis(methylamine) complex compared to that of the pentaammine complex. When this contribution is taken into account, the values of $\delta(\Delta G^*)$ are −39 kJ mol^{-1} and −34 kJ mol^{-1}, respectively, for Co(III) and Cr(III). These two numbers are approximately equal within the experimental errors of the kinetic studies. Moreover, it is clear that the major contribution to the differences in the behavior of Co(III) and Cr(III) is the much greater value of ΔH^* for $[Cr(NH_2CH_3)_5Cl]^{2+}$ as opposed to that obtained for $[Co(NH_2CH_3)_5Cl]^{2+}$. While the errors in ΔH^* are large, especially for the Co(III) complexes, the trend clearly points to a common dissociative conjugate base mechanism operating for both Co(III) and Cr(III).

Conclusions. A reexamination of the available evidence points to I_d mechanisms operating for the spontaneous aquations of both $[Co^{III}(NH_2R)_5X]^{n+}$ and $[Cr^{III}(NH_2R)_5X]^{n+}$ complexes, with similar activated states for the two metal ions. The kinetic differences are mainly attributable to the effects of π-bonding and the ionic radii of the metal ions in the ground state, rather than any inherent differences in the activated states. Similarly, the limiting S_N1CB mechanism applies equally well to the base hydrolyses of both Co(III) and Cr(III). It is also likely that the kinetic behavior of Rh(III), which is intermediate between Co(III) and Cr(III), may be due to ground-state rather than activated-state differences, and this aspect is currently being explored.

In hindsight, the enthalpy and entropy of activation give more mechanistic information than is generally recognized. It has been argued often that because ΔH^* and ΔS^* are not generally sensitive to whether or not Co(III) or Cr(III) is the metal ion involved in the substitution reaction, they are not useful for mechanistic assignments. However, the analysis described here indicates that these arguments were based on the false premise that the mechanisms of spontaneous aquations of Co(III) and Cr(III) are different.

Acknowledgment. The author is grateful for the helpful comments provided by Professor A. M. Sargeson and Associate Professor J. K. Beattie during the preparation of this paper and to Dr. T. W. Hambley for communicating the results of the molecular mechanics calculations. This work has been supported in part by the Australian Research Grants Scheme.

Registry No. $Cr(NH_2CH_3)_5Cl^{2+}$, 19418-71-4; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Co(NH_2CH_3)_5Cl^{2+}$, 30051-70-8; $Co(NH_3)_5Cl^{2+}$, 14970-14-0.

Contribution from the Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland, and Chemistry Department, University of Virginia, Charlottesville, Virginia 22903

Comparison of the Stabilities of Monomeric Metal Ion Complexes Formed with Adenosine 5′-Triphosphate (ATP) and Pyrimidine-Nucleoside 5′-Triphosphates (CTP, UTP, TTP) and Evaluation of the Isomeric Equilibria in the Complexes of ATP and CTP

Helmut Sigel,*[1a] Roger Tribolet,[1a] Raman Malini-Balakrishnan,[1a] and R. Bruce Martin*[1b]

Received November 26, 1986

Under experimental conditions where the self-association of the nucleoside 5′-triphosphates (NTPs) ATP, CTP, UTP, and TTP is negligible, potentiometric pH titrations were carried out to determine the stabilities of the $M(H{\cdot}NTP)^-$ and $M(NTP)^{2-}$ complexes, with $M^{2+} = Mg^{2+}$, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} ($I = 0.1$; 25 °C). These experiments were evaluated and combined with previous results from the same laboratory to obtain a large number of experimental data. The aim of this procedure was to generate reliable stability constants, especially for $M(NTP)^{2-}$, with a clearly defined error range. The stability of most of the $M(ATP)^{2-}$ complexes was significantly larger than that of the corresponding complexes formed with the pyrimidine-nucleoside 5′-triphosphates (PNTPs); this increased stability was attributed, in agreement with previous research, to the formation of macrochelates. The percentage of the macrochelated isomers in the $M(ATP)^{2-}$ systems was quantified by employing the difference $\log K^M_{M(ATP)} - \log K^M_{M(PNTP)}$: with the exception of $Ca(ATP)^{2-}$, which exists only as a phosphate-coordinated species, all mentioned $M(ATP)^{2-}$ complexes form to different extents macrochelates, $M(ATP)^{2-}_{cl}$ (e.g., $Cu(ATP)^{2-}_{cl}$ and $Zn(ATP)^{2-}_{cl}$ are formed to 67 ± 2% and 28 ± 7%, respectively). When earlier results of spectrophotometric studies are taken into account, it becomes evident that of the 56 ± 4% of $Ni(ATP)^{2-}_{cl}$ about 25% exists in the form of an outer-sphere macrochelate; i.e., a water molecule is between N-7 and the phosphate-coordinated Ni^{2+}. Similar reasoning and ^1H NMR shift measurements indicate that probably 11 ± 6% of $Mg(ATP)^{2-}$ is also present in aqueous solution in the form of such an outer-sphere-macrochelated isomer. Careful analysis of all available data indicates that inner- and outer-sphere forms of $M(ATP)^{2-}$ occur for Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} in comparable amounts; $Cu(ATP)^{2-}$ forms no outer-sphere species to any significant extent, and $Ca(ATP)^{2-}$ exists only in the open, phosphate-coordinated form. Of all $M(PNTP)^{2-}$ complexes only $Cu(CTP)^{2-}$ forms a base-back-bound species (32 ± 6%); this base back-binding is confirmed by UV difference spectroscopy. In a detailed analysis the isomeric equilibria occurring with $M(H{\cdot}NTP)^-$ complexes are evaluated; estimates for the formation degree of the isomers carrying the proton at the nucleic base residue or at the γ-phosphate group are given by taking into account also macrochelate formation where appropriate. As M^{2+}/NTP complexes are the substrates for many enzymic reactions, some possible biological implications of these results regarding selectivity are indicated.

Enzymic reactions involving[2] ATP and other NTPs are metal ion dependent,[3-8] the metal–NTP complexes being usually the substrates. This dependence explains the interest of many coordination chemists in these complexes; considering the metabolic importance of ATP, their efforts are also well justified. In the case of ATP, the most basic site at the adenine residue is N-1,[9]

---

[1] (a) University of Basel. (b) University of Virginia.

[2] Abbreviations: Ado, adenosine; AMP, adenosine 5′-monophosphate; ATP, adenosine 5′-triphosphate; CTP, cytidine 5′-triphosphate; Cyt, cytidine; dien, diethylenetriamine (=1,4,7-triazaheptane); M^{2+}, general divalent metal ion; NTP, nucleoside 5′-triphosphate; PNTP, pyrimidine-nucleoside 5′-triphosphate, i.e. CTP, UTP, or TTP; UTP, uridine 5′-triphosphate; TTP, thymidine 5′-triphosphate. The phosphate groups in the NTPs are labeled α, β, and γ, where the last refers to the terminal phosphate group.

[3] Cooperman, B. S. *Met. Ions Biol. Syst.* **1976**, *5*, 79–126.

[4] Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255–378.

[5] Mildvan, A. S. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1979**, *49*, 103–126.

[6] Eichhorn, G. L. *Met. Ions Biol. Syst.* **1980**, *10*, 1–21.

[7] Wu, F. Y.-H.; Wu, C.-W. *Met. Ions Biol. Syst.* **1983**, *15*, 157–192.

[8] Kalbitzer, H. R. *Met. Ions Biol. Syst.* **1986**, *22*, 81–103.

0020-1669/87/1326-2149$01.50/0