Coordination Chemistry Reviews, 94 (1989) 109–150
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MECHANISM OF THERMAL AND PHOTOCHEMICAL LIGAND SUBSTITUTION REACTIONS OF CHROMIUM(III) AND OTHER OCTAHEDRAL METAL COMPLEXES

L. MØNSTED

Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C (Denmark)

O. MØNSTED

Department of Inorganic Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø (Denmark)

(Received 25 July 1988)

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0010-8545/89/$14.70

A. INTRODUCTION

The substitution of ligands in metal complexes is a process of fundamental importance in a variety of contexts including many practical applications, and it has been the subject of several reviews. Some recent contributions include articles on thermal substitution of divalent and trivalent metal ions [1], on volumes of activation for solvent exchange [2], substitution and isomerization reactions [3] and on photochemical and photophysical processes of metal-centred transition metal excited states [4,5].

The present review will predominantly be concentrated on the reactivity of chromium(III) complexes in acidic aqueous solution with particular emphasis on the reactivity of simple monodentate ligands, on the effects from non-reacting ligands and on interaction with potential ligands in the second coordination sphere. The review will be based upon a personal selection of available data structured according to the types of approach used within this field of chemistry, and a particular attempt will be made at unifying the often contrasting or inconsistent literature views.

(i) Water ligand exchange in metal ions

Ligand substitution rates span a range from those which are diffusion controlled to those which are impractically slow. About 20 orders of magnitude of this range are illustrated in Fig. 1 for water ligand exchange of a number of hydrated and substituted metal ions. The figure shows a clear distinction between the transition metal ions and the main group metal ions. General trends in this latter category are easily seen; the metal ions all react fairly rapidly, many rates are close to the diffusion-controlled limit and there is a clear correlation between a decrease in the (charge/ionic radius) ratio of the metal ion and an increase in the rate of water ligand exchange. These observations point towards the significance of charge dipole contributions to the metal ligand bond stabilization for these metal ions.

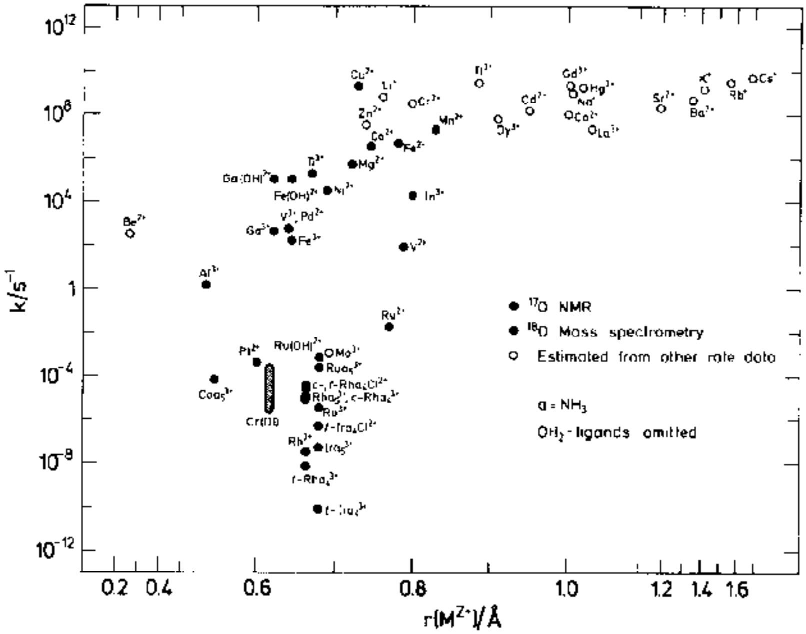


Fig. 1. Rate of water ligand exchange at 25 °C in aqua metal ions as a function of the effective metal ion radius. Ionic radii are from ref. 15. Most rate constants are from refs. 2 and 6 supplemented with data for chromium(III) from refs. 7–9 and 14, Rua_5^{3+}, Ru^{3+} and Ru^{2+} data from refs. 12 and 13, Rh(III) data from ref. 10 and Ir(III) data from ref. 11.

For the transition metal ions, however, a rate constant comparison between similar complexes having the same *d*-electron configuration

d^3: $Cr^{3+} < Mo^{3+}$

d^5: $Fe^{3+} > Ru^{3+}$

d^6: $Fe^{2+} > Ru^{2+}$, Rh(III) > Ir(III)

d^8: $Pd^{2+} > Pt^{2+}$

shows, except for the Cr^{3+}–Mo^{3+} pair, that the above trend with charge and radius is reversed, and as discussed later in this review, the probable cause for this derives from the operation of ligand field effects which increase with increasing atomic number for each pair.

(ii) Classification of ligand substitution mechanisms

Any successful mechanistic approach to reaction kinetic problems will require a description of the transition state of the process, and as this is not a chemical species which can be studied by conventional chemical methods, information on its properties is necessarily indirect. Comparative studies of both competitive reactivities of individual complexes and similar reactions of different complexes can provide clues to the characterization of the general features of the transition state.

Ligand substitution mechanisms are at present most commonly labelled according to whether the effect of bond breaking or the effect of bond formation is dominant. Stoichiometric mechanisms in which ligand dissociation or association takes place and where the consequences of an intermediate with either a reduced or an increased coordination number are apparent are labelled D and A respectively. The broad class of intimate mechanisms, where synchronous bond breaking and bond formation occur is labelled I for interchange supplemented with subindices d or a to signify the dominance of either a dissociative or an associative contribution to the properties, such as energy or volume, of the transition state [16]. One characteristic feature of the above classification scheme is the vaguely defined borders between the use of the different labels. This makes a stringent application difficult, and a comparative terminology involving (more/less) (associative/dissociative) is frequently adopted.

(iii) Effects of non-reacting ligands

Rate constants for ligand substitution reactions from about 10^3 s^{-1} and upwards are only accessible by relaxation methods, and this prerequisite that the systems be initially at equilibrium has severely limited the study of effects from the remaining coordination sphere on metal ion reactivity in this range of rates. Thus systematic studies of such effects are rare and have been mainly concentrated on the reactivity of robust complexes with four or five ammonia or other amine ligands. The data in Fig. 1 for Cr(III), Ru(III), Rh(III) and Ir(III) can be used to demonstrate that the coordination of even simple ligands may modify the metal ion reactivity of the simple aqua ions by several orders of magnitude.

(iv) Mechanisms of ligand substitution in chromium(III) complexes

Chromium(III) is probably the metal ion with the most varied coordination sphere in terms of donor atoms for which ligand substitution processes have been studied in detail in both the electronic ground state and in excited states. The insensitivity towards participation in redox reactions, a well-developed preparative chemistry and a robustness which usually allows monitoring of the thermal reactivity by classical methods have all contributed to the accumulation of the significant amount of data for reactions of com-

TABLE 1

Time evolution of the mechanism of substitution in the pentaamminechromium(III) series of complexes

Year	Article	Mechanistic assignment	Ref.
1972	Mechanistic Information from Pressure and Temperature Effects on the Rate of Transfer of Oxygen-18 from Aquopentaamminechromium(III) and -rhodium(III) Ions to Solvent Water.	Associative	17
1973	Pressure Effects upon the Rates of Aquation of Halopentaamminechromium(III) Ions: Evidence for an Associative Mechanism.	I_a	18
1976	The Effect of Ligand Environment on the Mechanism of Substitution at Chromium(III).	I_d	19
1977	Determination of the Mechanism for the Aquation of Cobalt(III) and Chromium(III) Pentaammine Complexes by Use of a Volume Profile Diagram.	I_a	20
1978	Linear Free Energy Relationships and Activation Volumes for Water Exchange Reactions as Measures of the Degree of Association in the Transition State for Octahedral Substitution Reactions.	Degree of association increases in the order $Co(NH_3)_5X$ $< Ir(NH_3)_5X$ $< Rh(NH_3)_5X$ $< Cr(NH_3)_5X$ $< Cr(OH_2)_5X$	21
1978	Angular Overlap Model Calculations on Transition State Structures for Chromium(III) Substitution Reactions.	Associative interchange mechanism.	22
1978	Kinetics and Mechanism of the Reaction of Phosphate (H_3PO_4 and $H_2PO_4^-$) with Aquopentaamminechromium(III).	Reactivity pattern of $Cr(NH_3)_5(OH_2)^{3+}$ intermediate between $Cr(OH_2)_6^{3+}$ and $Co(NH_3)_5(OH_2)^{3+}$	23
1982	Water Exchange of *mer*-Triamminetriaqua- and Amminepentaaquachromium(III). Kinetic *cis*-Effect of Ammonia vs. Water.	Associative interchange mechanism	9
1984	Aquation of Chloropentaammine and Chloropentakis(methylamine) Complexes of Cobalt(III) and Chromium(III): Comparative Activation Volumes and Mechanistic Implications.	I_a	24
1984	Interpretation of Kinetic Data for the Reaction of Azide with Aquapentaamminechromium(III) and the Reverse (Aquation) Reaction.	Borderline I_a/I_d mechanism	25
1985	Equilibration of Bromide with Pentaammineaquachromium(III) and the Mechanism of Substitution into Pentaammineaquachromium(III).	Associative, but less than in the pentaaquachromium(III) series.	26

TABLE 1 (continued)

Year	Article	Mechanistic assignment	Ref.
1986	Hydrolysis of Coordinated Trifluoromethanesulfonate from Cobalt(III), Rhodium(III), Iridium(III) and Chromium(III) Pentaamines.	Bond breaking leads bond making by a substantial margin.	27
1987	A Common Dissociative Interchange (I_d) Mechanism for the Aquations of Pentaamminechlorocobalt(III) and -chromium(III) Complexes.	I_d	28
1987	Aquation of Neutral Ligands from Pentaamminecobalt(III) and -chromium(III) Ions: Mechanistic Differentiation.	I_a	29

plexes of this metal ion during the last decades. Important mechanistic questions are, however, still unanswered and continuing controversies on the mechanistic description of substitution in the pentaamminechromium(III) series of complexes (see Table 1) exemplify well the current status.

B. FREE ENERGY COMPARISONS

(i) Correlations between ΔG and ΔG°*

Correlations between free energy changes for series of reactants have probably been the single most important approach in comparative mechanistic studies [30]. In coordination chemistry, substitution reactions within

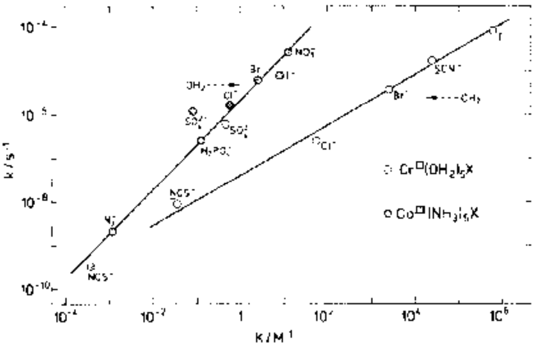


Fig. 2. Free energy correlation of rate and equilibrium data for substitution in pentaamminecobalt(III) and pentaaquachromium(III) complexes at 25°C and ionic strength $I = 1.0$ M. Cobalt(III) data: OH$_2$ 7 33; remaining ligands, 34. Chromium(III) data: OH$_2$ [35,36]; Cl$^-$ [37,38]; Br , I , NCS [32]; SCN$^-$ [38,39]; and SO$_4^{2-}$ [40,41].

the pentaamminecobalt(III) series of complexes were the first to be subjected to this treatment, and the linear correlation of the form

$$\log k_{-} \approx 1.00 \log K + (\text{constant}) \qquad (1)$$

for

$$\mathrm{Co^{III}(NH_3)_5X + OH_2 \underset{k_+}{\overset{k}{\rightleftarrows}} [Co(NH_3)_5(OH_2)]^{3+} + X} \qquad K = k_{-}/k_{+}$$

(see Fig. 2) unambiguously illustrated the importance of dissociative activation [31], with the anation rate constant k_+ insensitive to the nature of the entering X ligand.

Substitution in hexaaquachromium(III), however, behaves differently, and as is evident from the approximate correlation

$$\log k_{-} \approx 0.58 \log K + (\text{constant}) \qquad (2)$$

shown in Fig. 2, there is a significantly greater variation in the anation rate constants. If this approximately linear correlation is also accepted to reproduce the data adequately, then it can be taken to imply that the bonding between the chromium(III) centre and the reacting ligands in the transition state [32] is important.

The "linear free energy" correlations within the pentaamminecobalt(III) and pentaaquachromium(III) series of reactions represent extremes in the sense that other $\Delta G^{\ddagger}$ vs. ΔG° correlations for complex formation reactions have slopes between the values given by eqns. (1) and (2). This is shown in Fig. 3 for substitutions in the pentaamminechromium(III) series of complexes, for which the free energy correlation has a slope of 0.69 [21].

This difference between the pentaaquachromium(III) and the pentaamminechromium(III) series therefore shows that not only the identity of the central metal ion but also the non-reacting ligands are important for the mechanistic classification of ligand substitution processes. This is discussed later with reference to the free energies of activation of the two series of complexes of chromium(III).

Various theoretical and semiempirical approaches to the detailed interpretation of free energy correlations and the interplay between free energy changes and structure have appeared [51]. Some particularly simple considerations are depicted in Fig. 4 for the reaction

$$\mathrm{ML_5X + Y \rightleftarrows ML_5Y + X}$$

where X is varied and Y kept constant leading to

$$\alpha \approx (\delta\,\Delta G^{*}/\delta\,\Delta G^{\circ})_{\mathrm{X=Y}} \approx (1 + \Delta G^{*}_{\mathrm{YY}}/G_{\mathrm{Y}})/2$$

for a linear free energy correlation of the form

$$\log k \quad \approx \alpha \log K + (\text{constant})$$

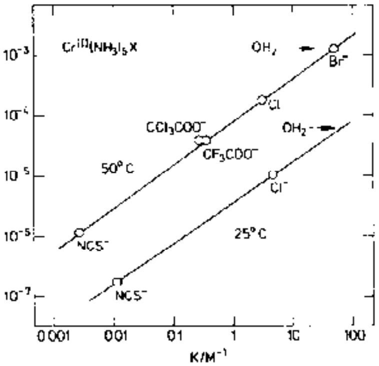


Fig. 3. Free energy correlation of rate and equilibrium data for substitution in pentaamminechromium(III) complexes at 25 and 50 °C and ionic strength $I = 1.0$ M. Data at 25 °C: OH_2 [7]; Cl^- [18,43]; NCS^- [43,44]. Data at 50 °C: OH_2 [7]: NCS^-, CCl_3COO^-. CF_3COO^- [43]; Cl^- [26,43]; Br^- [21,26,43].

As $0 \leqslant \Delta G^{*}_{YY} \leqslant G_Y$, limits for α, corresponding to $1/2 \leqslant \alpha \leqslant 1$, are predicted, which interestingly enough for such a simple approach are in agreement with the values found so far for reactivity comparisons of this type. One consequence of the form of the curves in Fig. 4 is, that in order to have a positive free energy of activation, significant loss in energy by stretching the M–X bond prior to energy gain by M–Y bond formation is required.

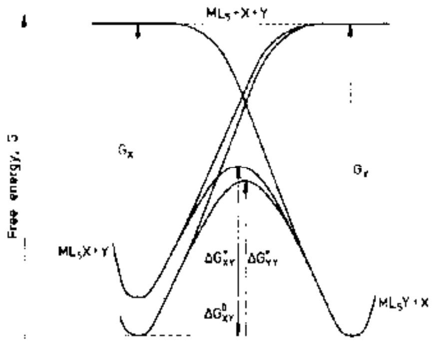


Fig. 4. Free energy profile for metal–ligand bond energy contributions for the ligand substitution process: $ML_5X + Y \rightarrow ML_5Y + X$. G_X and G_Y are free energies of dissociation to $ML_5 + X + Y$ for reactants and reaction products respectively. ΔG^{*}_{XY} and ΔG^{*}_{YY} are free energies of activation for the reactions $ML_5X + Y$ and $ML_5Y + Y$ respectively. Free energies for binding of X and Y along the reaction coordinate are assumed proportional, and the free energy of the system is assumed to be the sum of contributions from the two reacting ligands.

(ii) Free energy correlations and data for water exchange

Solvent participation in a chemical reaction presents a conceptual problem for mechanistic comparisons involving data for both solvent exchange and other chemical reactions. Second-order rate constants obtained by division of the observed first-order rate constants by the solvent concentration have been claimed not to be useful [52], with reference to the frequently assumed two-step mechanism for ligand exchange, i.e. the diffusion-controlled formation of an encounter complex in a solvent cage followed by first-order ligand exchange. For anation–hydrolysis reactions this gives a reaction scheme which is usually formulated as

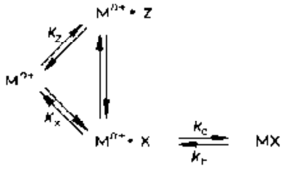
$$MOH_2 + X \overset{K_X}{\rightleftarrows} MOH_2 \cdot X \underset{k_h}{\overset{k_a}{\rightleftarrows}} MX(\cdot OH_2) \tag{3}$$

If the encounter complex is thought of as the metal ion and its second coordination sphere then the K_X equilibrium in eqn. (3) is of course undefined for a solvent exchange reaction.

Empirically it is possible from Figs. 2 and 3 to calculate what may be termed the "effective" water concentration, i.e. that value of K which correlates the data for the water exchange rates with the data for the remaining reactions. This gives the following values: $[Co(NH_3)_5(OH_2)]^{3+}$, 2.4 M; $[Cr(NH_3)_5(OH_2)]^{3+}$, 66 M (25°C) and 50 M (50°C); $[Cr(OH_2)_6]^{3+}$, 1400 M. The trend in these values is seen to follow the degree of association in the transition state as determined by current criteria.

(iii) Free energy correlations and ion pair formation

The reaction scheme (3) is not strictly appropriate in a constant ionic medium where larger amounts of an inert electrolyte are present with the purpose of keeping the ionic atmosphere around the reactants constant. If anation of a cation M^{n+} with X^- takes place in a medium with an inert Z^- anion and the cation–anion interactions are dominated by 1 : 1 electrostatic interactions between the anions and the higher charged cations, then the reaction scheme (3) is modified to



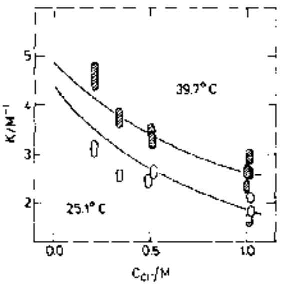


Fig. 5. Inner sphere equilibrium constant for

$$cis\text{-}[\mathrm{Cr(cyc}b)(\mathrm{OH_2})_2]^{3+} + \mathrm{Cl}^- \rightleftarrows cis\text{-}[\mathrm{Cr(cyc}b)(\mathrm{OH_2})\mathrm{Cl}]^{2+} + \mathrm{OH_2}$$

as a function of chloride concentration (cyc*b* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [53]. Experimental points are drawn with an extent corresponding to plus–minus the estimated uncertainties and the solid curves are calculated from parameters determined from these equilibrium data and kinetic data for the equilibration process. (Reproduced with permission from Acta Chem. Scand., ref. 53.)

If $C_M \ll (C_X + C_Z)$, which is the common experimental situation, experimental constants, k_- and K, for this scheme may be expressed as

$$k_- \approx k_b$$

and

$$1/K \approx (k_a/k_b)\{K_X/(1 + K_X C_X + K_Z C_Z)\}$$

Unless $K_x \approx K_Z$, this functional relationship is indicative of a non-constant ionic medium, and several such examples may be found in the literature.

Thus the inner sphere equilibrium constant for

$$cis\text{-}[\mathrm{Cr(cyc}b)(\mathrm{OH_2})_2]^{3+} + \mathrm{Cl}^- \rightleftarrows cis\text{-}[\mathrm{Cr(cyc}b)(\mathrm{OH_2})\mathrm{Cl}]^{2+} + \mathrm{OH_2}$$

was found to vary according to $K(\mathrm{obs}) \approx K_0/(1 + K_1[\mathrm{X}])$ as function of the ionic medium composition in 1.00 M (H,Na)(ClO_4,Cl). This correlation can be derived from the data given in Fig. 5. Also the controversy concerning the equilibrium constant for

$$[\mathrm{Cr(NH_3)_5(OH_2)}]^{3+} + \mathrm{Br}^- \rightleftarrows [\mathrm{Cr(NH_3)_5Br}]^{2+} + \mathrm{OH_2}$$

was traced back to the difficulty of keeping the ionic medium constant. The kinetically determined constant from the intercept/slope ratio of a k_{obs} vs. [Br^-] plot has a value of 0.21 M^{-1} [19] which was an order of magnitude larger than the value of 0.019 M^{-1} [21] determined by chemical analysis. The "kinetic value" was influenced by preferential ion pair formation of the chromium(III) containing cations with bromide rather than perchlorate in the 1.00 M (H,Na)(ClO_4,Br) solutions [26].

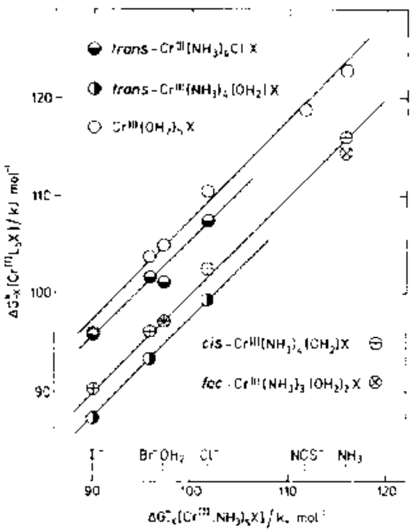


Fig. 6. Correlation of free energies of activation for substitution in chromium(III) complexes. References: OH_2, a [35,36], b c d e [7]; NH_3, a [42] b c [46] c [50]; Cl^-, c d g [47]; Br^-, b [18,48] c d [48] g [47]; I^-, b [18,45] c [48,49] g [49] where a = $Cr^{III}(NH_3)_5X$ series, b = $Cr^{III}(OH_2)_5X$ series, c = *cis*-$Cr^{III}(NH_3)_4(OH_2)X$ series, d = *trans*-$Cr^{III}(NH_3)_4(OH_2)X$ series, e = *fac*-$Cr^{III}(NH_3)_3(OH_2)_2X$ series, g = *trans*-$Cr^{III}(NH_3)_4ClX$ series. (Reproduced with permission from Acta Chem. Scand., ref. 7.)

(iv) Correlations between free energies of activation

The previously discussed data for substitution within the pentaamminechromium(III) and the pentaaquachromium(III) series of complexes show a clear distinction between the substitution kinetic behaviour of these

TABLE 2

Single-ligand reactivity parameters, $\Delta G^*(X)$, at 25° C, for aquation of chromium(III) complexes (see eqn. (4) and Fig. 6) and the corresponding rate constant ratios

X	$\Delta G^*(X) - \Delta G^*(OH_2)$ (kJ mol^{-1})	k_X/k_{OH_2}
I^-	−7	17
Br^-	−1	1.5
OH_2	0	1
Cl^-	+6	1/11
NCS^-	+14	1/280
NH_3	+18	1/1400

two series of chromium(III) complexes, the current explanation being a greater degree of associative behaviour within the pentaaquachromium(III) than the pentaamminechromium(III) series of reactants. However, this interpretation does not accord with the data in Fig. 6 which illustrates that ΔG^{*}_{-X} for hydrolysis in the pentaaqua series is linearly correlated with ΔG^{*}_{-X} for hydrolysis in the pentaammine series: the line drawn has a slope of 1.00. This correlation also holds for the series of the other chromium(III) reactants included in Fig. 6, so that in all these cases, reacting ligands must be bound in a similar fashion in the transition state. These last linear correlations have been used as the basis for separating the free energies of activation for hydrolysis reactions into two terms. One of the terms depends on the substituted ligand and the other on the non-reacting ligands [7], i.e.

$$\Delta G^{*}(\mathrm{Cr^{III}L_5X}) \approx \Delta G^{*}(\mathrm{Cr^{III}L_5}) + \Delta G^{*}(\mathrm{X}) \qquad (4)$$

The results of this treatment are shown in Table 2.

C. VOLUMES OF ACTIVATION

(i) Activation volumes for water exchange reactions

The effect of pressure on the rate of ligand substitution has been interpreted most successfully for reactions with no net change in volume. In Fig. 7 are shown data for water exchange in a number of aqua metal ions. Some major trends are immediately apparent: the smaller the cation size and charge the more positive is the volume of activation, and cations with known tendencies to form complexes with a lower coordination number than the ordinary aqua ion such as Co^{2+}, for which a tetraaqua ion has been characterized [54], Ni^{2+}, Al^{3+} etc., have generally positive volumes of activation for water exchange. These trends accord with the volumes of the transition states being significantly more similar than are the volumes of the precursor aqua metal ions.

Negative volumes of activation for water exchange in hexaaquachromium(III), $\Delta V^{*} \approx -9.3$ cm^3 mol^{-1}, and pentaammineaquachromium(III), $\Delta V^{*} \approx -5.8$ cm^3 mol^{-1} [36,17] in contrast with $\Delta V^{*} \approx +1.2$ cm^3 mol^{-1} for water exchange in pentaammineaquacobalt(III) [33], have been used to assign an associative interchange mechanism to the first two reactions and a dissociative interchange mechanism to the cobalt(III) reaction. In this context the correlation between volumes of activation for water exchange and the proportionality parameter from linear free energy correlations [21] (see Fig. 8) is also relevant.

Evidently the interpretation of activation volumes is based upon a model for the volume change on going from reactants to the transition state and

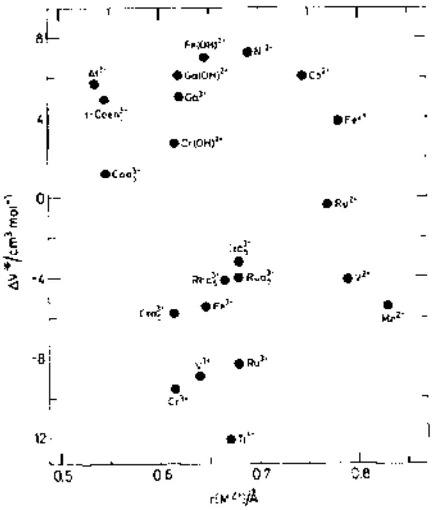


Fig. 7. Volumes of activation for water exchange in different aqua ions as a function of the effective ionic radii. Volumes of activation are from refs. 2 and 3 except for Rua$_5^{3+}$, Ru^{2+} and Ru^{3+} which are from refs. 12 and 13. Ionic radii are from ref. 15.

several approaches have been attempted. It was suggested early on that the coordinated metal ions had the same volume in the ground states as in the transition state [55], independent of whether this had an increased or reduced coordination number. This assumption has as a consequence limit-

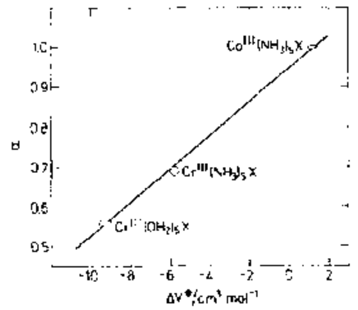


Fig. 8. Correlation between volumes of activation for water exchange in [ML$_5$(OH$_2$)]$^{3+}$ complexes and slopes of linear free energy relationship for reactions of M^{III}L$_5$X complexes (see Figs. 2 and 3). Experimental values are indicated by contour ellipses of the probability density function drawn at the 68% probability level. (Reproduced with permission from Acta Chem. Scand., ref. 21).

ing volumes of activation corresponding to $+18.07$ cm^3 mol^{-1}, the molar volume of water, for a limiting dissociative process and -18.07 cm^3 mol^{-1} for a limiting associative process. This analysis was supported by data for substitution in a series of pentaamminecobalt(III) complexes [20], but has been questioned [56] partly with reference to the semiempirical equation [57]

$$V_{\text{abs}} + n_c 18.07 \approx 2.523(r+\Delta r)^3 - 4.175z^2/(r+\Delta r) \qquad (5)$$

which rather accurately reproduces the "absolute volumes", relative to $V(\mathrm{H}^+) \approx -5.4$ cm^3 mol^{-1}, of a significant number of aqua metal ions of ionic radius r, charge z, and coordinated with n_c water ligands in the first coordination sphere, when Δr is taken as 2.387 Å. Equation (5) in combination with the known increase in ionic radii with increasing coordination number [15] limits the activation volume range to values numerically less than 12–14 cm^3 mol^{-1} [58].

(ii) Activation volumes for reactions accompanied by volume changes

The detailed interpretation of activation volume data for reactions accompanied by volume changes is particularly ambiguous when annihilation or creation of charge is involved. For uncharged ligands the situation seems less complicated and the dissociative interchange mechanism for pentaamminecobalt(III) complexes has been substantiated by a linear correlation involving volumes of activation and partial molar volumes of reactants and

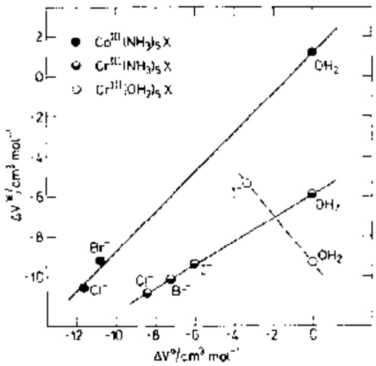


Fig. 9. Volumes of activation as a function of change in volumes of reaction for the reaction $\mathrm{M^{III}L_5X + OH_2 \rightarrow [ML_5(OH_2)]^{3+} + X}$. A slope of 0.51 for the ΔV^{*} vs. ΔV° correlation in the pentaamminecobalt(III) series of reactants is reported in ref. 61. This is, however, obtained by averaging the pressure-dependent volumes of activation in ref. 59. The present data at zero pressure are from refs. 18, 35, 36, 59 and 62.

reaction products for a series of uncharged leaving ligands [60]. For series of reactions of pentaamminecobalt(III) [59] and pentaamminechromium(III) involving charged ligands [18], linear correlations between volumes of activation and volumes of reaction with slopes of 1.0 and 0.60 respectively, shown in Fig. 9, have been interpreted analogously to the similar free energy relations.

For pentaaquachromium(III) complexes, however, a comparison between the data for water exchange in the hexaaqua [35,36] ion and iodide ligand aquation from the pentaaquaiodo complex [62] (see Fig. 9) is clearly seen not to be in agreement with the above interpretation. Also there is a large difference between the volumes of activation for stereoretentive water exchange and isomerization, $+5.7$ cm^3 mol^{-1} [63] and $+13.2$ cm^3 mol^{-1} [64] respectively, in *trans*-diaquabis(1,2-ethanediamine)cobalt(III). This difference is interpreted as resulting from a tetragonal pyramidal vs. a trigonal bipyramidal transition state, both with reduced coordination numbers, which points towards very significant effects not included in the present semiempirical rationalizations.

(iii) Solvational effects on volumes of activation

The volume of activation for

$$[\mathrm{Co(NH_3)_5Br}]^{2+} + \mathrm{OH_2} \rightarrow [\mathrm{Co(NH_3)_5(OH_2)}]^{3+} + \mathrm{Br^-}$$

changes from -8.7 cm^3 mol^{-1} in 0.01 M $HClO_4$ to $+12.0$ cm^3 mol^{-1} in 0.01 M $HClO_4$ $+0.8$ mM sodium poly(ethylene) sulphonate [65]. This large effect makes it difficult to accept a simple rationalization of volume changes predominantly in terms of intrinsic effects during the formation of the transition state.

The forced disruption of the structure of the second solvation sphere which results when the transition state or the reactive intermediate is formed will influence the second-sphere volume, and this will depend on whether second-sphere solvent reorganization is fast enough to take place during the time of the ligand substitution process. If such reorganization does not occur, then a dissociative process may be expected to be accompanied by a decrease in molar volume of the second-sphere solvent, corresponding to an increased pressure in this region around the metal ion, and for an associative process the opposite effect may be expected. For hexaaquachromium(III) it has been determined that 12–16 water molecules are present in the second solvation sphere [66], and significant contributions to the volume of activation may therefore result when solvent reorganization is too slow to reconstitute an equilibrium solvent structure around the reactive intermediate during the time of reaction. The tendencies in the literature to map a

($\Delta V^* > 0/\Delta V^* < 0$) experimental result for exchange processes into an (I_d/I_a) mechanistic classification should consequently be viewed with some circumspection.

D. EFFECTS OF NON-REACTING LIGANDS

(i) Ligand substitution in pentaammine vs. pentakis(methaneamine) complexes

Replacement of five water ligands with five ammonia ligands in the first coordination sphere around a chromium(III) centre is demonstrated to have a profound influence on the mechanistic assignment of the substitution reactions at the sixth coordination position. Substitution with five methaneamine ligands causes even more pronounced differences and detailed considerations and comparisons of rates and activation parameters for chloride ligand aquation of the pentaamine complexes

$$[(\mathrm{am})_5\mathrm{MCl}]^{2+} + \mathrm{OH}_2 \rightarrow [(\mathrm{am})_5\mathrm{M(OH}_2)]^{3+} + \mathrm{Cl}^-$$

where M = Cr(III), Co(III) or Rh(III) and am = NH_3 or CH_3NH_2, have substantiated the view of dissociative activation for the cobalt(III) reactions and varying degrees of associative behaviour for the chromium(III) and rhodium(III) reactions [24,67,68].

This interpretation has recently been questioned with reference to structural details and arguments concerning the effect of π-bonding between the metal centre and the chloride ligand [28,69], and the suggestion was made that all the reactions occurred by dissociative activation. This view was subsequently opposed with reference to a comparative study of volumes of activation for aquation of a significant number of neutral ligands from pentaamminecobalt(III) and pentaamminechromium(III) complexes [29].

A key issue in the arguments in refs. 28, 69 and 70 is a comparison between the metal–chloride bond lengths in the pentaamminechloro and pentakis(methaneamine)chloro complexes. This is shown in Table 3. The trend in bond length differences could be correlated with the trend in associative behaviour as displayed by the volumes of activation for water exchange in the pentaammineaqua complexes, but it has been argued in refs. 28, 69 and 70 that any observed differences are functions of ground state properties only, and that no significant interaction exists between the metal and the reacting ligands in the transition state. Lack of structural details of the transition state obviously leaves much space for interpretational freedom but it is not immediately obvious why differences in the transition state properties indicated by other criteria are disregarded. This, together with the fact that metal–chloride bond distances even in the ground state probably vary with the type and concentration of the anions in solution, thus

TABLE 3

Kinetic data for chloride ligand aquation in pentaammine and pentakis(methaneamine) complexes and metal chloride bond lengths

Reactant complex	10^6k (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	d(M–Cl) (Å)	Ref.
$[Co(NH_3)_5Cl]^{2+}$	1.67 (25.0 °C)	96(1)	−44(3)	2.286(2)	74, 73
$[Co(CH_3NH_2)_5Cl]^{2+}$	39.6 (25.0 °C)	95(1.5)	−10(4)	2.283(1)	24, 71
$[Rh(NH_3)_5Cl]^{2+}$	48.0 (84.9 °C)	101.5(1.2)	−46(3)	2.356(1)	68, 70
$[Rh(CH_3NH_2)_5Cl]^{2+}$	24.0 (84.9 °C)	101.9(9)	−50(2)	2.339(1)	68, 70
$[Cr(NH_3)_5Cl]^{2+}$	8.70 (25.3 °C)	93.3(0.4)	−28.9(1.3)	2.327(1)	67, 72
$[Cr(CH_3NH_2)_5Cl]^{2+}$	0.261 (25.3 °C)	110.0(0.4)	−2.1(1.3)	2.299(1)	(24, 67), 28

reflecting the change with anion type in the solid state as discussed below, makes mechanistic conclusions from the bond length distances in Table 3 doubtful.

(ii) Solid state structural data applied to dissolved species

Structural data on complexes in solution are not readily obtained, and it is mainly for hydrated metal ions that such data exist. As a result of this lack of information, solid state structures are frequently supposed to be maintained in solution but even for robust metal complexes this is only a valid approximation as far as the overall geometry is concerned. Thus bond lengths vary as a function of the external environment in the solid state and it is not clear what effect can be expected upon dissolution. The distribution of 33 cobalt(III)–chloride bond lengths in various salts of the *trans*-dichlorobis(1,2-ethanediamine)cobalt(III) cation is shown in Fig. 10. From these data it is not obvious what effect a solvent will have upon a particular bond length, but the spread in bond length values seen for this cation is probably not an unreasonable estimate of the uncertainty of the average bond length in solution as compared with its value in a solid state structure. For different complexes there is, as expected, an even greater spread of values as shown by the distributions of cobalt(III)–chloride and chromium(III)–chloride bond lengths in Fig. 10.

(iii) Kinetic trans *effect*

The kinetic *trans* effect for substitution reactions of octahedral metal complexes is considerably less well established than that for substitution in

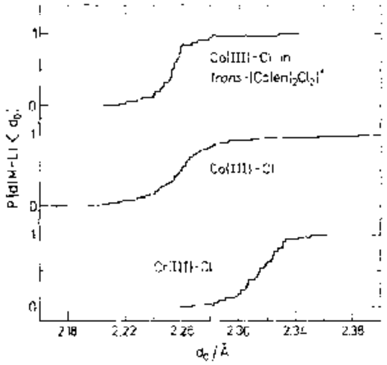


Fig. 10. Cumulative distribution function for solid state metal(III) chloride bond lengths in *trans*-dichlorobis(1,2-ethanediamine)cobalt(III), in chlorocobalt(III) and in chlorochromium (III) complexes. Data for 33, 82 and 34 bond lengths respectively for "Werner-type" complexes are found in the Cambridge Crystallographic Data Base [75].

square-planar complexes, particularly in those of platinum(II) [16]. Unambiguous data are mainly available for chromium(III) and rhodium(III) complexes and for both metal ions the "*trans* directing" function of ligands increases along the series $OH_2 < NH_3 < Cl^- < Br^- < I^-$. This reactivity order is based upon data for aquation of coordinated chloride in aquachlororhodium(III) complexes [76], for ligand substitution [77,78] including water exchange [10] in tetraaminerhodium(III) and pentaaminerhodium(III) complexes, and for water exchange in ammineaquachromium(III) [7–9] and pentaaquahalochromium(III) complexes [14,79]. Data for reactions involving no net change in free energy are most unambiguously comparable and a comparison of data for selected water exchange reactions of chromium(III) and rhodium(III) is shown in Table 4. As demonstrated in this table, the kinetic *trans* effect series is the same as the nephelauxetic series [80] but this is as yet unexplained. However, the significantly larger effect for the low spin d^6 configuration of rhodium(III) than for the d^3 configuration of chromium(III) has been rationalized on the basis of ligand field effects of the *trans* ligand [10]. The ligand field contribution of the *trans* ligand, ΔL_T^*, to the free energy of activation is given by the difference in ligand field stabilization of the transition state and the ground state, and to a good approximation this is given by

$$\Delta L^*_{T[Cr(III)]} \approx (1/5)\left(\Delta^{GS}_{T[Cr(III)]} - \Delta^{TS}_{T[Cr(III)]}\right)$$

and

$$\Delta L^*_{T[Rh(III)]} \approx (2/5)\left(\Delta^{GS}_{T[Rh(III)]} - \Delta^{TS}_{T[Rh(III)]}\right)$$

TABLE 4

Comparison of free energies of activation at 25 °C for water exchange in some chromium(III) and rhodium(III) complexes

Trans ligand	Cr(III) complex	ΔG^* (kJ mol^{-1})	Ref.	Rh(III) complex	ΔG^* (kJ mol^{-1})	Ref.
OH_2	$[Cr(OH_2)_6]^{3+}$	105.04 ± 0.12	35, 36	*trans*-$[Rh(NH_3)_4(OH_2)_2]^{3+}$	119.50 ± 0.17	10
NH_3	$[Cr(OH_2)_5(NH_3)]^{3+}$	99.0 ± 0.3	9	$[Rh(NH_3)_5(OH_2)]^{3+}$	102.00 ± 0.05	17
Cl^-	$[Cr(OH_2)_5Cl]^{2+}$	98.9 ± 0.2	14	*trans*-$[Rh(NH_3)_4Cl(OH_2)]^{2+}$	98.55 ± 0.07	10

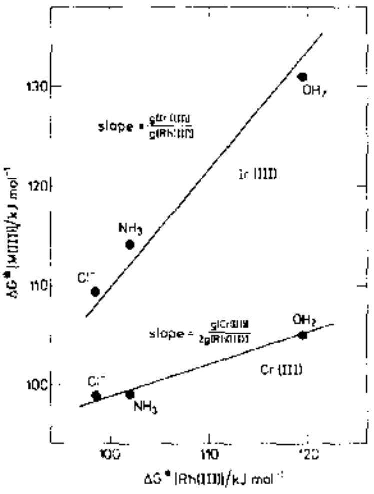


Fig. 11. Correlation between kinetic *trans* effect of water, ammonia and chloride in the chromium(III) and rhodium(III) complexes of Table 4 and of iridium(III) complexes of ref. 11. The straight lines are drawn with slopes calculated from the non-kinetic *g* parameters of ref. 81: $g[Cr(III)] \approx 208$ kJ mol^{-1} (1.74 μm^{-1}), $g[Rh(III)] \approx 323$ kJ mol^{-1} (2.70 μm^{-1}) and $g[Ir(III)] \approx 383$ kJ mol^{-1} (3.20 μm^{-1}).

The Δ values may to a reasonable approximation be separated into a metal-dependent (M) and a ligand-dependent (T) part [81]:

$$\Delta_{T[M]} \approx f[T]\, g[M]$$

Using this partition and assuming the same relative change in parameters for chromium(III) and rhodium(III) on going from the ground state to the transition state, the *trans*-ligand-independent ratio is given by

$$\Delta L^*_{T[Cr(III)]}/\Delta L^*_{T[Rh(III)]} \approx g[Cr(III)]/2g[Rh(III)] \qquad (6)$$

As seen in Fig. 11 this approximation describes rather well the metal-ion-dependent differences between the chromium(III) and rhodium(III) complexes in Table 4. New data for water exchange in *trans*-$Ir^{III}(NH_3)_4X(OH_2)$ complexes, where $X = OH_2$, NH_3 or Cl^- [11], have also been included in the figure and are seen to be in agreement with the above rationalization and a suitably modified form of eqn. (6).

(iv) Kinetic cis effect of water vs. ammonia

Only a few unambiguous systematic studies exist of the effect of ligand variations in a position *cis* to the reacting ligand. Data for water exchange in

TABLE 5

Summary of kinetic parameters for water exchange in $[Cr(NH_3)_x(OH_2)_{6-x}]^{3+}$ species, $0 \leqslant x \leqslant 5$, classified according to the ligands in positions *trans* and *cis* to the reacting water ligand. The data are from refs. 7–9

cis	*trans* NH_3			*trans* OH_2		
	10^5k (s^{-1})	ΔH^* ($kJ\ mol^{-1}$)	ΔS^* ($J\ K^{-1}\ mol^{-1}$)	10^5k (s^{-1})	ΔH^* ($kJ\ mol^{-1}$)	ΔS^* ($J\ K^{-1}\ mol^{-1}$)
$\{(NH_3)_4\}$	5.75 ± 0.06	99.1 ± 1.4	$+7 \pm 5$	1.17 ± 0.03	98.5 ± 2.1	-9 ± 7
$\{(NH_3)_3(OH_2)\}$	5.92 ± 0.13	95.1 ± 1.9	$+7 \pm 6$	1.23 ± 0.05	–	–
cis-$\{(NH_3)_2(OH_2)_2\}$	5.78 ± 0.09	95.1 ± 1.3	-7 ± 5	1.02 ± 0.09	105 ± 4	$+13 \pm 14$
trans-$\{(NH_3)_2(OH_2)_2\}$	7.6 ± 1.0	–	–	0.997 ± 0.013	97.0 ± 1.1	-15 ± 4
$\{(NH_3)(OH_2)_3\}$	4.9 ± 0.4	101 ± 3	$+11 \pm 9$	0.449 ± 0.014	–	–
$\{(OH_2)_4\}$	2.8 ± 0.4	–	–	0.246 ± 0.012	109.6 ± 1.3	$+16 \pm 5$

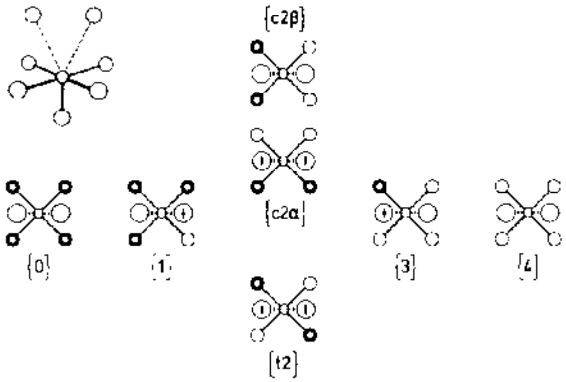


Fig. 12. Idealized transition state geometry used to rationalize the kinetic *cis* effect for water exchange in ammineaquachromium(III) complexes. Upper left: perspective drawing of the transition state geometry. Lower right: possible combinations of two different types of ligands in a position *cis* to the two reacting ligands. Reacting ligands influenced by different nearest *cis* ligands are marked with ⦶. (Reproduced with permission from Acta Chem. Scand., ref. 9.)

chromium(III) complexes coordinated with the possible combinations of water and ammonia ligands classified according to the *trans* ligand and the combination of *cis* ligands are shown in Table 5. The pattern of reactivity accompanying successive substitution of NH_3 for OH_2 in a position *cis* to the reacting ligand is independent of the *trans* ligand. This has been rationalized with reference to ligand–ligand interactions between the *cis* ligands and both the entering and the leaving ligand in a transition state having the geometry shown in Fig. 12 [9]. Interactions between *cis* ligands of different types and the entering or leaving ligand can be expected to give transition states of lower symmetry and of lower energy than predicted by a linear function of the number of *cis* ligands of a particular type. If only interactions between the reacting ligands and the two nearest *cis* ligands in a rigid square-pyramidal unit of metal and non-reacting ligands are considered, then the relative stabilization energies, from Fig. 12, are 1 : 2 : 2 : 1 for $\{(NH_3)_3(OH_2)\}$: *cis*$\{(NH_3)_2(OH_2)_2\}$: *trans*-$\{(NH_3)_2(OH_2)_2\}$: $\{(NH_3)(OH_2)_3\}$ combinations of *cis* ligands. Figure 13 illustrates that this simple model can describe the actual experiments rather well.

(v) Steric effects from cis *ligands*

Rate retardation for substitution at a chromium(III) centre by the introduction of bulky ligands *cis* to the reacting ligand has already been

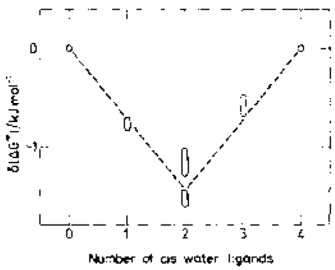


Fig. 13. Kinetic *cis* effect for complexes with less than tetragonal symmetry of the *cis* ligands. The data are calculated from those of Table 5 as differences between actual free energies of activation and free energies of activation interpolated as a function of the number of *cis* water or ammonia ligands, i.e.

$$\delta\,(\Delta G^{*}) = \Delta G^{*}\left(cis\text{-}(NH_3)_{4-i}(OH_2)_i\right) - ((4-i)/4)\,\Delta G^{*}\left(cis\text{-}(NH_3)_4\right)$$
$$-\,(i/4)\,\Delta G^{*}\left(cis\text{-}(OH_2)_4\right)$$

Average data for water and ammonia in positions *trans* to the reacting water ligand are given, drawn with a vertical extent corresponding to plus–minus the estimated uncertainty. (Reproduced with permission from Acta Chem. Scand., ref. 9.)

described for the pentaammine vs. pentakis(methaneamine) data. Similar trends are also noted for rigidly coordinated polyamines with a 2,6-diazaheptane unit coordinated via the nitrogen atoms. Kinetic data for some

TABLE 6

Kinetic parameters for chloride ligand aquation of some *trans*-tetraaminedichlorochromium(III) complexes in acidic aqueous solution

Tetraamine [a]	Medium	$10^6 \times k$ (25 °C) (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	Ref.
$(NH_3)_4$	1 M $(Na,H)ClO_4$	45 ± 3	88.9 ± 1.2	29 ± 4	47, 92
(en)(tn)	0.4 M HNO_3	19.3 ± 0.9	95 ± 2	15 ± 7	83
$(me_2tn)_2$	0.1 M HNO_3	22.0 ± 0.5	100.9 ± 1.3	+5 ± 4	84
$(tn)_2$	0.1 M HNO_3	20.7 ± 0.6	99.8 ± 1.4	−1 ± 5	85
$(tn)_2$	1 M $(Na,H)ClO_4$	9.9 ± 1.0	107n ± 2	+19 ± 6	86
meso-2,3,2-tet	Dilute HNO_3	3.2 ± 0.3	104 ± 2	−4 ± 6	87
rac-3,2,3-tet	0.1 M HNO_3	1.06 ± 0.08	91.9 ± 1.3	−50 ± 4	88
cyclam	0.01 M HNO_3	0.026 ± 0.012	113 ± 3	−9 ± 10	89
meso-3,3,3-tet	0.1 M HNO_3	7.4 ± 0.9	102 ± 2	−2 ± 8	82
meso-3,3,3-tet	1 M $(Na,H)CF_3SO_3$	6.3 ± 0.8	102 ± 2	−2 ± 6	82

[a] Abbreviations for ligand names: en = 1,2-ethanediamine, tn = 1,3-propanediamine, me_2tn = 2,2-dimethyl-1,3-propanediamine, 2,3,2-tet = 1,4,8,11-tetraazaundecane, 3,2,3-tet = 1,5,8,12-tetraazadodecane, cyclam = 1,4,8,11-tetraazacyclotetradecane.

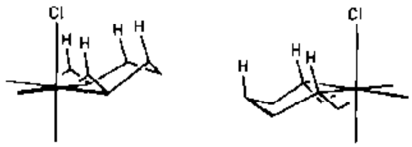


Fig. 14. Axial hydrogen atoms in the direction of the two differently coordinated chloride ligands in (*RS*)-*meso-trans*-[Cr(tntntn)Cl$_2$]$^+$. The situation to the left applies to both chloride ligands in (*RRSS*)-*trans*-[Cr(cyclam)Cl$_2$]$^+$. Ligand name abbreviations are defined in Table 6. (Reproduced with permission from Acta Chem. Scand., ref. 82.)

trans-tetraaminedichlorochromium(III) complexes are shown in Table 6. The strongly reduced reactivity of both chloride ligands in the cyclam complex and of one of the chloride ligands in the tntntn complex has been rationalized by reference to an increase in the steric interactions in the direction of the reacting ligand [82] (see Fig. 14), supporting the view of interaction between the metal centre and both the leaving ligand and the entering ligand in the transition state.

(vi) Reactions accompanied by stereochemical change

Thermal reactions of chromium(III) are predominantly stereoretentive, a feature once considered to be characteristic of chromium(III) reactions compared with cobalt(III) reactions. This is now known to be incorrect and a significant number of racemization, isomerization and other reactions accompanied by configurational changes have been characterized for chromium(III). Configurational change, however, characteristically has only been found to occur for species with coordinated water ligands, and this is compelling though indirect evidence that these reactions occur as the result of a non-stereoretentive water ligand exchange. Examples of reactions in this category are the racemization of *cis*-$[Cr(en)_2(OH_2)_2]^{3+}$ [90] and the isomerization of $[Cr(NH_3)_x(OH_2)_{6-x}]^{3+}$ ($x = 2, 3, 4$) [42,50] and $[Cr(NH_3)_x(OH_2)_{4-x}Cl_2]^+$ complexes ($x = 0, 1, 2, 3$) [91–93].

E. PHOTOINDUCED LIGAND SUBSTITUTION REACTIONS

Robust metal complexes have played a fundamental role in the experimental and theoretical development of excited state substitutional reactivity. Complexes of chromium(III) were among the first to be studied and formed the major experimental background for the first attempt to rationalize empirically the photochemical reactivity and photostereochemistry of this class of compounds in terms of ligand field parameters [94]. This work stimulated considerable experimental effort, and in the following years many

TABLE 7

Solvent effects on excited state chloride and ammonia ligand substitution rates in $[Rh(NH_3)_5]Cl^{2+}$ at 25 °C. Data from ref. 96.

Solvent	$10^{-6}k(Cl^-)$ (s^{-1})	$10^{-6}k(NH_3)$ (s^{-1})	$\frac{k(Cl^-)}{k(NH_3)}$	ϕ(total) (mol einstein^{-1})
Water	12.7	1.4	9	0.20
Formamide	2.5	< 0.5	> 5	≈ 0.068
Methanol	< 0.46	< 5.6	0.07	0.118
N,*N*-Dimethylformamide	< 0.17	0.82	< 0.2	≤ 0.035
Dimethyl sulphoxide	0.12	2.2	0.06	0.074

new compounds were prepared and investigated photochemically. It soon became apparent, however, that many of these compounds, particularly with coordinated fluoride ligands, did not adhere well to the original rationalizations and that a new theoretical foundation was needed. Several approaches were attempted and these culminated in a ligand field rationalization based on an angular overlap model with particular focus on the σ- and π-binding abilities of the ligands [95]. This resolved the apparent anomalies associated with coordinated fluoride but at the expense of a significantly more complicated model.

Although theoretical approaches to photochemical problems are still predominantly centred around models based on a ligand field concept, the recently demonstrated strong solvent dependence, particularly on the photochemical chloride ligand solvolysis rate, of the pentaamminechlororhodium(III) ion [96] (see Table 7) certainly points towards the importance of solvent effects and does not encourage the use of photochemical models based only upon a ligand field concept.

(i) Photosubstitution of coordinated water

In spite of the large efforts put into the photochemical research of transition metal complexes during the last decades, only very few investigations of water ligand photosubstitution have appeared. The photochemical reactivity of hexaaquachromium(III) was studied first [97] and was found to occur with a rather small quantum yield. A later investigation of pentaammineaquarhodium(III) resolved the question of the apparently anomalous photoinertness of this complex by demonstrating that photochemical water exchange occurred with a rather high quantum yield [98] of 0.43(3) mol einstein^{-1}. Results which supplement this limited information are water ligand substitution quantum yields for the isomeric $[Rh(NH_3)_4(OH_2)Cl]^{2+}$ [99], $[Rh(NH_3)_4(OH_2)_2]^{3+}$ [100] and $[Rh(en)_2(NH_3)(OH_2)]^{3+}$ [101] com-

TABLE 8

Quantum yields and estimated standard deviations (mol complex einstein^{-1}) for the photochemical reactivities of ammineaquachromium(III) complexes in 0.5 M $HClO_4$ + 0.5 M $NaClO_4$ at 25°C irradiated at 546 nm. The reported data are ϕ(exch) for apparently stereoretentive water exchange, ϕ(isom) for stereomobile water exchange, $\phi(NH_3)$ for ammonia ligand substitution and ϕ(total) for the total photochemical reactivity

Reactant complex	ϕ(exch) [a]	ϕ(isom) [a,b]	$\phi(NH_3)$ [b]	ϕ(total)
$[Cr(NH_3)_6]^{3+}$		–	0.443(15) [c]	0.443(15) [c]
$[Cr(NH_3)_5(OH_2)]^{3+}$	0.078(10)	–	0.195(8)	0.273(13)
cis-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.057(9)	0.141(6)	0.058(9)	0.256(15)
trans-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.001(3)	0.310(4)	0.025(8)	0.336(9)
fac-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	0.040(16)	0.146(5)	0.053(7)	0.239(17)
mer-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	~ 0.12(3) [d]	0.064(4)	0.011(5)	0.19(3)
cis-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	~ 0.179(15) [d]	0.000(1)	0.0019(2)	0.181(15)
trans-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	0.072(16)	0.051(2)	0.0041(8)	0.127(18)
$[Cr(NH_3)(OH_2)_5]^{3+}$	~ 0.057(4) [d]	–	0.0000(1)	0.057(4)
$[Cr(OH_2)_6]^{3+}$	0.019(2) [e]	–	–	0.019(2)

[a] Ref. 102. [b] Ref. 103. [c] Ref. 110, λ_{irr} = 366 nm. [d] These values contain contributions from different types of coordinated water ligands. [e] Ref. 97.

plexes and for the series of ammineaquachromium(III) complexes [102,103].

Data for the latter series of complexes are exhibited in Table 8, and these data were particularly informative in relation to the semiempirical predictions for the leaving ligand. Preferred water ligand substitution over substitution of coordinated ammonia in *cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ is seen from the data in Table 8. This is in agreement neither with the leaving ligand being that of the highest ligand field strength on the axis of lowest average ligand field strength [94] nor with the more elaborate excited state so-called "bond indices", I^*, calculations which give $I^*(NH_3(eq)) < I^*(OH_2) < I^*(NH_3(ax))$ [95]. Both treatments predict preferred photochemical ammonia ligand substitution.

(ii) "Antithermal" behaviour of photochemical reactions

The fact that thermal and photochemical reactions of chromium(III) often give different reaction products has been termed as "antithermal" behaviour of the photochemical processes. This was demonstrated early on for pentaamminechlorochromium(III) which thermally releases coordinated chloride apparently with retention of configuration to give pentaammineaquachromium(III), but photochemically gives *cis*-tetraammineaquachlorochromium(III) [104] probably as the result of aquation of the ammonia ligand in the position *trans* to the chloride ligand in the reactant

TABLE 9

Comparison of data for competitive photochemical and thermal reactions of selected ammineaquachromium(III) complexes

Reactant	Reaction products	ϕ [a] (mol einstein^{-1})	k(50 °C) [b] (s^{-1})	ΔH* (kJ mol^{-1})
trans-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	*trans*-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	0.071 ±0.012 [c]	(89 ± 3)×10^{-5} [c]	97.0±1.1
	cis-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	0.051 ±0.002	(0.43± 0.04)×10^{-6}	113 ±4
	$[Cr(NH_3)(OH_2)_5]^{3+}$	0.0041±0.0008	(1.61± 0.06)×10^{-6}	107.2±1.6
fac-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	*fac*-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	0.040 ±0.016 [c]	(366 ±15)×10^{-5} [c]	95.1±1.3
	cis-$[Cr(NH_3)_2(OH_2)_4]^{3+}$	0.041 ±0.005	(0.62± 0.04)×10^{-6}	112.6±2.4
cis-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	*cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	0.078 ±0.010 [c]	(250 ±16)×10^{-5} [c]	95.1±1.9
	fac-$[Cr(NH_3)_3(OH_2)_3]^{3+}$	0.031 ±0.006	(2.35± 0.12)×10^{-6}	104.7±2.0
$[Cr(NH_3)_5(OH_2)]^{3+}$	$[Cr(NH_3)_5(OH_2)]^{3+}$	0.078 ±0.010	(137 ± 6)×10^{-5}	99.1±1.4
	cis-$[Cr(NH_3)_4(OH_2)_2]^{3-}$	0.175 ±0.006	(4.03± 0.16)×10^{-6}	110.5±1.6

[a] Data from refs. 102 and 103. [b] Extrapolated from data for 60–80 °C in ref. 46 and data for 15–40 °C in refs. 7 and 8. [c] These data are not statistically corrected but refer to the total reactivity of the complex: ϕ(complex) = $n\phi(OH)_2$ for a "$Cr(OH_2)_n$" complex (see ref. 7).

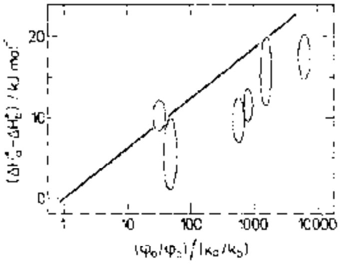


Fig. 15. Correlation between photochemical and thermal data for some competitive reactions of chromium(III). The solid line corresponds to $(\phi_a/\phi_b)/(k_a/k_b)_T = \exp((\Delta H_a^* - \Delta H_b^*)/RT)$, $T = 323$ K. The experimental data are shown as contour ellipses of the probability density function drawn at the 68% level. (Reproduced with permission from Acta Chem. Scand., ref. 102.)

complex [105]. Many such analogous examples have subsequently been found, and it has been suggested that photosubstitution generally occurs by *trans* attack of the entering ligand, corresponding to a so-called "edge displacement" [106] on passing from reactant to reaction product.

Stereoretentive thermal reactions of chromium(III) are known generally to have lower energies of activation than reactions in which a stereochemical change occurs. This could obviously invalidate assignments of the photochemical reaction as "antithermal", but it was not until recently that data for competitive thermal and photochemical reactions allowing quantitative comparisons were available [102,103]. These data are shown in Table 9 from which it is clear that for two competing reactions labelled a and b, the reaction with the higher activation enthalpy is invariably more dominating photochemically than thermally, i.e. $\phi_a/\phi_b > k_a/k_b$ when $\Delta H_a^* > \Delta H_b^*$.

This is further elaborated in Fig. 15, where it is shown that a good correlation exists between the $(\phi_a/\phi_b)/(k_a/k_b)$ ratio and the difference in enthalpies of activation. Clearly this trend is not evidence for "antithermal" behaviour, and it has been rationalized by a mechanism in which a key step is intersystem crossing between an excited quartet state of comparable energy and the ground state in a pentagonal bipyramidal transition state or in an intermediate resulting from *trans* attack of an entering water molecule (see Fig. 16). A schematic drawing of the variation of ground state and lowest excited state energy levels along the reaction coordinate is shown in Fig. 17 for this mechanism.

(iii) Predictions of photochemical reactivities

Data for the competitive reactions of the ammineaquachromium(III) complexes [102] were rationalized within the above mechanism, and product

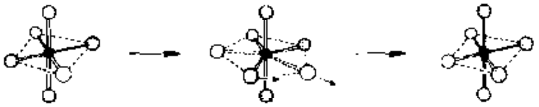


Fig. 16. *Trans* attack of a water molecule in *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ forming *cis*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ stereospecifically via a pentagonal bipyramidal transition state or reactive intermediate. (Reproduced with permission from Acta Chem. Scand., ref. 102.)

distributions showed that (i) water ligands were predominantly the leaving ligands, and (ii) the reactivity was predominantly occurring in that plane of the octahedral complex which contained the largest number of water ligands. Furthermore, some preference for entry of the incoming water ligand in a position *cis* to a coordinated ammonia ligand was noted. Point (i) was rationalized with reference to data for thermal reactions and point (ii) was correlated with the relative ligand field strengths of coordinated water vs. ammonia, and should therefore also apply to other systems.

Product distributions of the photochemical reactions of the isomeric tetraamminedifluorochromium(III) complexes have been investigated in detail [107]. Substitution of coordinated ammonia is obviously preferred over substitution of coordinated fluoride which is not unreasonable from a comparison of relevant thermal data [108]. If the suggested correlation of point (ii) with ligand field strength holds then *cis*- and *trans*-tetraamminedifluorochromium(III) should be expected to react predominantly in the *cis*- and in the *trans*-$\{(NH_3)_2F_2\}$ plane respectively. Consequently, *cis*-tetraamminedifluorochromium(III) is predicted to give both 1,2,6-triammine-4-aqua-3,5-difluorochromium(III) and 1,2,6-triammine-3-aqua-4,5-difluoro-

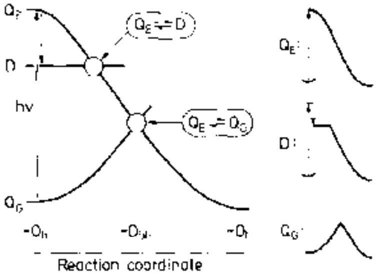


Fig. 17. Schematic variation of ground state and lowest excited state energy levels along the reaction coordinate for the *trans* attack mechanism in Fig. 16. Inserts show energy variations along the reaction coordinate by reactions of the lowest quartet Q_E and doublet D excited states and the quartet ground state Q_G respectively. (Reproduced with permission from Acta Chem. Scand., ref. 102.)

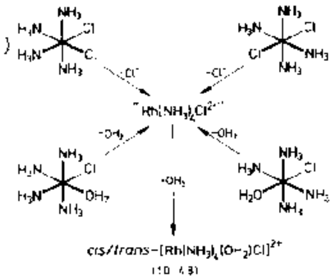


Fig. 18. Excited state chemical deactivation reactions of *cis*- and *trans*-tetraamminеaquachlororhodium(III) and *cis*- and *trans*-tetraamminedichlororhodium(III) isomers within a limiting dissociative reactivity model.

chromium(III) as main reaction products. The latter isomer should dominate as reaction product in the photolysis of the *trans* tetraamminedifluorochromium(III) isomer. These predictions are all in agreement with the data in ref. 107.

(iv) Intimate mechanism for photoinduced ligand substitution

Detailed competition studies have been the basis for assigning a dissociative mechanism to photosubstitution in rhodium(III) complexes. A particularly illustrative example is the photochemical formation of tetraammineaquachlororhodium(III) isomers, which takes place with a constant *cis/trans* ratio independent of reactant geometry and independent of whether formation occurs by water exchange in tetraammineaquachlororhodium(III) or chloride ligand aquation in tetraamminedichlororhodium(III) [109]. This is shown in Fig. 18, and it has been proposed that the intermediate of reduced coordination number has the geometry of a square pyramid and that equilibration between chloride in the apical and basal position is fast compared with deactivation.

Chromium(III) complexes do not behave in an analogous fashion as is evident from the very different *cis/trans* ratios for the formation of tetraamminediaquachromium(III), shown in Table 10. Rhodium(III) complexes of higher charge also do not conform to simple dissociative behaviour, as shown by the differences in competition ratios for the tripositive reactants in Table 10. Stereoretentive contributions are seen to be disfavoured relative to those expected for a limiting dissociative behaviour, and therefore competitive equilibration and deactivation of square-pyramidal intermediates with different apical ligands do not explain these results. In a stereochemical sense the behaviour of these rhodium(III) reactions is intermediate between

TABLE 10

Quantum yields and estimated standard deviations (mol einstein^{-1}) for competitive formation of *cis* and *trans* isomers of some rhodium(III) and chromium(III) complexes

Reactant	Leaving ligand	ϕ_{cis}	ϕ_{trans}	$\frac{\phi_{trans}}{\phi_{cis}}$	Ref.
cis-$[Rh(NH_3)_4Cl_2]^+$	Cl^-	0.063(7)	0.328(9)	5.3(5)	99
trans-$[Rh(NH_3)_4Cl_2]^+$	Cl^-	0.025(9)	0.122(9)	5(2)	109
cis-$[Rh(NH_3)_4(OH_2)Cl]^{2+}$	OH_2	0.12(3)	0.543(14)	4.5(6)	99, 109
trans-$[Rh(NH_3)_4(OH_2)Cl]^{2+}$	OH_2	0.074(2)	0.33(4)	4.5(6)	109, 99
cis-$[Rh(NH_3)_4(OH_2)_2]^{3+}$	OH_2	0.041(4)	0.102(4)	2.5(4)	100
trans-$[Rh(NH_3)_4(OH_2)_2]^{3+}$	OH_2	0.0111(7)	0.0143(11)	1.30(17)	100
cis-$[Rh(en)_2(NH_3)Cl]^{2+}$	Cl^-	0.0705(19)	0.0042(10)	0.060(16)	101
trans-$[Rh(en)_2(NH_3)Cl]^{2+}$	Cl^-	0.075(3)	0.000(4)	0.00(5)	101
cis-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$	OH_2	0.33(2)	0.113(6)	0.35(3)	101
trans-$[Rh(en)_2(NH_3)(OH_2)]^{3+}$	OH_2	0.276(12)	0.05(2)	0.18(8)	101
$[Cr(NH_3)_5(OH_2)]^{3+}$	NH_3	0.175(6)	0.020(6)	0.11(3)	103
cis-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	OH_2	0.057(9)	0.141(6)	2.5(4)	102, 103
trans-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	OH_2	0.310(4)	0.001(3)	0.00(2)	103, 102

that of the rhodium(III) complexes of lower charge and that of the chromium(III) complexes.

A possible cause for this change in stereochemistry could be competition between excited state chemical deactivation and exchange of potential ligands between the second coordination sphere and bulk solvent. As shown

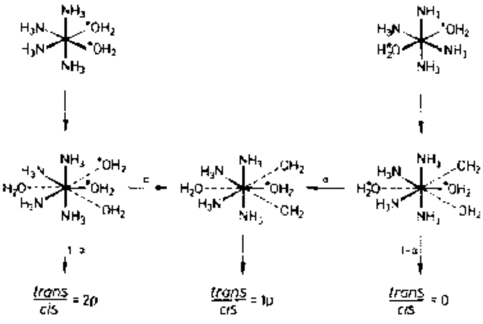


Fig. 19. Suggested chemical deactivation pathways for *cis*- and *trans*-tetraamminediaquarhodium(III) excited states. Probability of second-sphere solvent water exchange in the reactive trigonal bipyramidal intermediate is labelled α, and the product *trans*/*cis* formation ratio ρ. The close similarity of this scheme and that of Fig. 18 for $\alpha = 1$ should be noted, as should its similarity to the mechanism of Fig. 16 for $\alpha = 0$.

in Fig. 19 this could explain the results in terms of a common mechanism for the different types of rhodium(III) complexes, and probabilities for ligand exchange in the second coordination sphere during the lifetime of the reactive intermediate are estimated to $\alpha \approx 1.0$ for the lower charged rhodium(III) complexes and to $\alpha \approx 0.65$ and $\alpha \approx 0.63$ respectively for the triply charged pairs of rhodium(III) complexes in Table 10. It should further be noted that this model for the photochemical reactivity of octahedral metal complexes can also account for the solvent dependence of the photochemical reactivity of the pentaamminechlororhodium(III) ion, as there is a clear correlation between the quantum yield ratio for loss of uncharged ammonia vs. negatively charged chloride (see Table 7) and the solvent dielectric constant.

F. THEORETICAL APPROACHES TO THE MECHANISM OF LIGAND SUBSTITUTION

In accordance with the mechanistic approach to the classification of ligand substitution mechanisms discussed at the beginning of this review, i.e. the view that detailed information on the transition state for a ligand substitution reaction is only indirectly available through experimental investigation, various theoretical approaches have been attempted for an increased understanding of this type of chemical process.

(i) Rationalization of empirical correlations between kinetic and spectroscopic data

Robustness vs. lability with respect to ligand substitution in transition metal ions was realized at an early stage to be correlated with the metal ion electronic configuration [111], and later calculations of ligand field contributions to enthalpies of activation for different transition state geometries of increased or reduced coordination numbers have partly quantified the qualitative trends in terms of parameters derived from spectroscopic data [112,113].

However, despite the considerable number of empirical correlations between kinetic and spectroscopic parameters which, particularly for complexes of chromium(III), have appeared in the literature, only a few of these have been interpreted in other than qualitative terms. The empirical correlation between enthalpies of activation for aquation processes of the type

$$\mathrm{Cr^{III}J_5X + OH_2 \rightarrow [CrJ_5(OH_2)]^{3+} + X} \qquad \mathrm{J = OH_2, NH_3}$$

and single-ligand Δ_X parameters [120], shown in Fig. 20, have, however, been analysed in some detail with reference to the transition state geometries

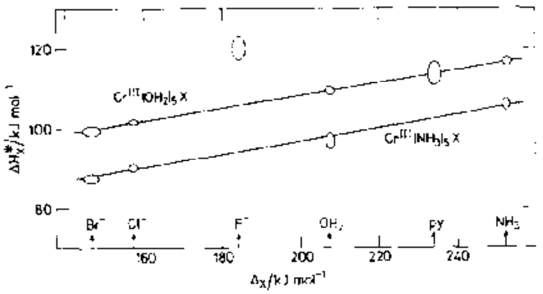


Fig. 20. Linear correlation between enthalpies of activation for X-ligand aquation in pentaaquachromium(III) and pentaamminechromium(III) complexes and spectroscopic Δ_X parameters. Experimental data are drawn as contour ellipses of the probability density function drawn at the 68% level. References: Br$^-$, a [114] b [43,45,118]; Cl$^-$, a [37] b [45,117,118]; F$^-$, a [37]; OH$_2$, a [36] b [17]; pyridine, a [115]; NH$_3$, a [46,116] b [46,119] where a = Cr^{III}(OH$_2$)$_5$X series and b = Cr^{III}(NH$_3$)$_5$X series. (Reproduced with permission from Acta Chem. Scand., ref. 22.)

shown in Fig. 21, Δ_X being the one-electron energy difference between the $e_g(O_h)$ and $t_{2g}(O_h)$ orbitals in an octahedral MX_6 complex. Results were almost identical for these geometries, and values of ϕ between 80° and 100°, depending on the assumed spectroscopic parameters of the entering and leaving ligand in the transition state, all quantitatively reproduced the experimental slopes of Fig. 20 [22]. One aspect of these calculations is the insensitivity of the ground state energy to Δ separations into Δ_σ and Δ_π contributions for almost all the transition state structures investigated. Except for the octahedral wedge transition state geometry in Fig. 21 with unrealistically large values of ϕ, only $\Delta = \Delta_\sigma - \Delta_\pi$ was found to be significant for the ground state energy, and hence for the ligand field contribution to the enthalpy of activation.

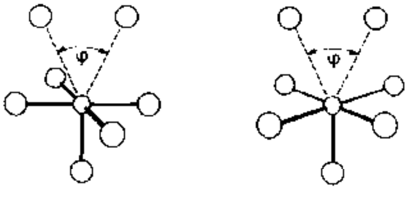


Fig. 21. Transition state geometries used to rationalize the empirical correlation in Fig. 20. Rotation of the two reacting ligands 45° around the four-fold axis of the ML_5 square-pyramidal unit of the metal and non-reacting ligands transforms the one geometry into the other.

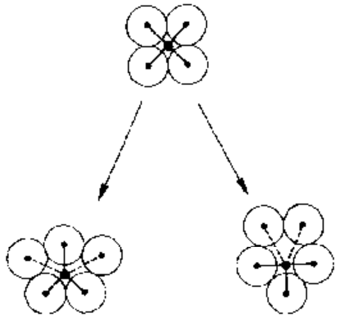


Fig. 22. Simulated transition state geometry for a two-dimensional solvent exchange process (cf. ref. 121) (left). Assumed two-dimensional transition state geometry for solvent exchange with a larger ligand–metal–ligand angle deformation potential (see text) (right).

(ii) Solvent exchange simulations

Computer simulation of solvent exchange in a hypothetical two-dimensional case [121] has shown that this process involves a collective motion of both the first and the second solvation sphere, and that the entering and leaving ligands are separated by a solvent molecule in the first coordination sphere, i.e. the substitution process occurs by a *trans* attack. The model applied to these simulations includes a metal–solvent radial interaction potential but no solvent–solvent interactions except as hard discs. Introduction of an angular solvent–metal–solvent potential with octahedral ligand positions of lowest energy should intuitively be expected to increase the possibility of *cis* attack of the entering ligand and this has been verified by more detailed considerations [122]. A pictorial representation of these two possibilities is shown in Fig. 22.

(iii) Ligand field contributions to enthalpies of activation for ligand substitution of metal ions with d^3 *and* d^6 *electronic configurations*

For transition metal ions the ligand field introduces an angular potential dependent upon the electronic configuration and ligand field strength. Such consequences of the ligand field are eminently suited for angular overlap model calculations [123], and some representative examples of ligand field contributions to enthalpies of activation for substitution in metal ions with either a d^3 or a d^6 electronic configuration are shown in Fig. 23.

The general trends of these results can be summarized as follows:

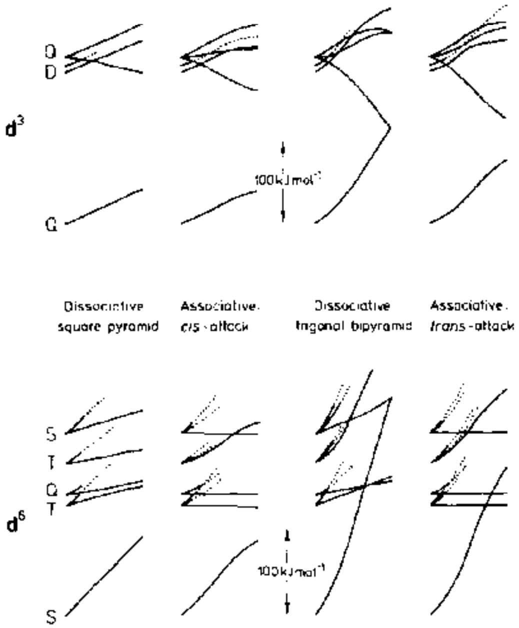


Fig. 23. Calculated variation of ground state and selected lower excited state energies along the reaction coordinate for a ligand exchange process of an octahedral metal complex: $ML_6 + L$ with a d^3 or d^6 electronic configuration. Transition state geometries for the dissociative processes are the regular polyhedra with identical values of $\Delta_\sigma(L)$ and $\Delta_\pi(L)$ for all the ligands. For the associative processes, the transition state geometries shown in Fig. 22 are supplemented with two ligands on a line perpendicular to the paper plane through the metal atom. The two reacting ligands have $\Delta_\sigma = 0.5\Delta_\sigma(L)$ and $\Delta_\pi = 0.5\Delta_\pi(L)$ in the transition state. Ligand field and angular parameters for structures along the reaction coordinate have been obtained by linear interpolation between the ground state and transition state values. Ligand field parameters are $\Delta_\sigma(L) \approx 2.04\ \mu M^{-1}$ and $\Delta_\pi(L) \approx 0.32\ \mu m^{-1}$ for the d^3 calculations [120] and $\Delta_\sigma(L) \approx 2.10\ \mu m^{-1}$ and $\Delta_\pi(L) \approx 0.00\ \mu m^{-1}$ for the d^6 calculations simulating water exchange in hexaaquachromium(III) and ammonia exchange in hexaamminecobalt(III) respectively. Interelectronic repulsion parameters B and C were taken as 0.07 μm^{-1} and 0.35 μm^{-1} respectively for both electronic configurations. Electronic states are labelled Q and D respectively for quartet and doublet states of the d^3 electronic configuration and S, T and Q respectively for singlet, triplet and quintet states of the d^6 electronic configuration. Calculations were performed using the methods described in refs. 123 and 126.

1. Ligand field effects do not discriminate between associative and dissociative transition states or intermediates. Energy variations along the reaction coordinate are very similar for the two modes of activation. Strong discrimination is, however, seen between stereoretentive reactions, *cis* attack

or a square-pyramidal transition state, and reactions accompanied by stereochemical change, *trans* attack or a trigonal bipyramidal transition state.

2. The ligand field gives a positive contribution to the enthalpies of activation for substitution reactions in the electronic ground state for both d^3 and d^6 metal complexes. The magnitude of the contributions is greater for greater Δ values of the involved ligands, and is considerably smaller for stereoretentive reactions than for reactions accompanied by stereochemical change. For a metal ion with a d^6 electronic configuration this latter difference may partly be compensated for by a spin change along the reaction coordinate (see ref. 124).

3. There is only a small ligand field contribution to enthalpies of activation for reactions of metal ions with a d^3 electronic configuration in the lowest excited doublet state and for metal ions with a d^6 electronic configuration in the lowest excited triplet or quintet state, and this is independent of any detailed transition state geometry.

4. There is a negative ligand field contribution to enthalpies of activation for reactions of a metal ion with a d^3 electronic configuration in the lowest excited quartet state. The numerical value of this contribution is greater for greater Δ values of the involved ligands and is numerically smallest for stereoretentive reactions.

This summary of the general trends in ligand field contributions to the energetics of ligand substitution processes provides a fair rationale of many general observations.

Thus ground state reactions of the relevant metal ions are slow (see Fig. 1) and this is generally accepted to be caused mainly by a large activation enthalpy with significant contributions from the ligand field. As an example the empirical correlation in Fig. 20 extrapolated to zero ligand field strength predicts water exchange in the hexaaquachromium(III) ion to be slowed down by a factor of 6×10^5 by the ligand field.

Opposing effects from ligand–ligand repulsion which tend to move ligands as far away from each other as possible and ligand field effects which for the ground states of the electronic configurations discussed here, oppose ligand movements away from the octahedral positions, make detailed stereochemical predictions difficult. There are trends, however, in available data which could suggest greater contributions to the overall rate from reactions accompanied by stereochemical change for complexes coordinated with ligands of low ligand field strength. Significant reactivity contributions from *cis/trans* isomerization between tetraaquadichlorochromium(III) isomers [91,93] and the lack of correlation between volumes of activation for iodide ligand aquation in pentaaquachromium(III) and water exchange in hexaaquachromium(III) (see Fig. 9) are two such examples.

Excited state reactions are orders of magnitude faster than the ground state reactions, but a clear distinction is seen between reactions of doublet excited chromium(III) and also of triplet excited rhodium(III), which both generally have measurable lifetimes in the microsecond to nanosecond time range, and quartet excited state chromium(III) for which the excited state lifetime is too small to be measured and has an upper limit of less than a few picoseconds [125].

The change in stereochemistry for chromium(III) substitution reactions between predominantly stereoretentive ground state reactions and excited state reactions which are accompanied by stereochemical change is easily understood on the basis of the differences in ligand field stabilization energies. The similarity between the ligand field calculations in Fig. 23 and the suggested mechanism for chemical excited state deactivation in Fig. 17 is relevant not only for the suggested pentagonal bipyramidal transition state with the entering and leaving ligands in the equatorial plane (Fig. 16) but also for a trigonal bipyramidal transition state or intermediate. Provided the lifetime of this latter species is low enough not to allow exchange of the leaving ligand between the second coordination sphere and bulk solvent (see Fig. 19 and the discussion thereof), also the stereochemical predictions of these two possibilities are similar to each other.

(iv) Ligand field predictions of photochemical reactivity

The general trends of ligand field effects on ligand substitution processes apparent from Fig. 23 can be further elaborated for complexes of lower symmetry than octahedral. As an example, calculations for fluoride and ammonia ligand substitutions in *cis*-tetraamminedifluorochromium(III) are shown in Fig. 24. The photochemistry of this complex has previously been discussed in relation to the empirical rationalizations of the photochemical reactivity of the ammineaquachromium(III) complexes, and the calculations for Fig. 24 have been made for a process with the maximum negative ligand field contribution to the activation enthalpy for an excited quartet state reaction. For simplicity and in view of the similarity of results for dissociative and associative processes a trigonal bipyramidal transition state geometry has been adopted.

Figure 24 clearly does not show a significant difference between aquation of a fluoride or an ammonia ligand, supporting the view that the leaving ligand cannot be predicted from spectroscopic parameters [102]. What is clearly seen, however, is that excitation to the low energy component of the

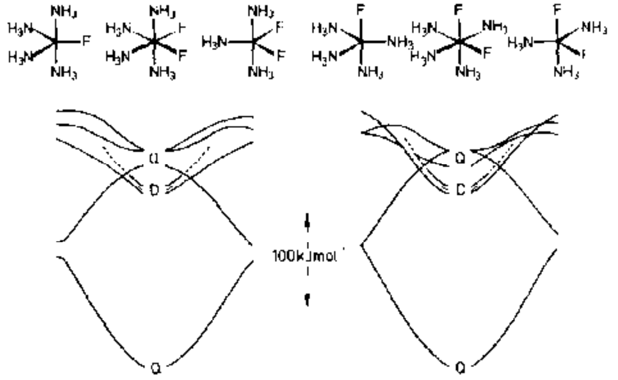


Fig. 24. Calculated variation of ground state and selected excited state energies along the reaction coordinate for fluoride and ammonia ligand aquation of the *cis*-$\{(NH_3)_2F_2\}$ and $\{(NH_3)_3F\}$ planes respectively of *cis*-tetraamminedifluorochromium(III). $\Delta_\sigma(F^-) \approx 2.22$ μm^{-1}, $\Delta_\pi(F^-) \approx 1.68$ μm^{-1}, $\Delta_\sigma(NH_3) \approx 2.10$ μm^{-1} and $\Delta_\pi(NH_3) \approx 0.00$ μm^{-1} [120]. Further details for the calculations are described under Fig. 23.

$^4T_2(O_h) \leftarrow {}^4A_2(O_h)$ transition promotes reactivity in the *cis*-$\{(NH_3)_2F_2\}$ plane, contrary to excitation to the doubly degenerate high energy component which promotes reactivity in the $\{(NH_3)_3F\}$ plane. Excited doublet state reactivity is predicted to occur via back intersystem crossing along the reaction coordinate to the excited quartet of comparable or lower energy and the probability of this occurring efficiently depends upon a small quartet-to-doublet energy separation. Both excited quartet and doublet reactions therefore favour reactivity of that plane of the octahedral complex with the lowest average value for the ligand Δ parameters, in agreement with the analysis of experimental results for the ammineaquachromium(III) complexes.

G. CONCLUSION

The application of currently accepted mechanistic criteria to ligand substitution processes in octahedral complexes in solution gives mechanistic labels highly influenced by the overall reactant charge and the non-reacting ligands. This results in an apparently increasing I_a character with increasing charge, cf. the reported mechanistic differences between reactions in acidic and basic solution, and an apparently increasing I_d character with an increasingly hydrophobic coordination sphere. These variations for a fixed metal centre are not readily explained within simple bonding theories and it is suggested that the effects arise from differences in electrostatic interactions between the reactive intermediate or transition state and the second coordination sphere.

The process of ligand substitution in an octahedral metal complex may thus be visualized as follows. There is a weakening of the bond between the metal centre and the leaving ligand with a simultaneous strengthening of the bond to one or more potential ligands in the second coordination sphere. Structural changes in the moiety of the central metal atom and the non-reacting ligands seem to be governed by ligand field effects, and the bonds to selected ligands in the second coordination sphere are predominantly electrostatic, i.e. are dominated by charge–charge or charge–dipole interactions. The observable consequences of this mode of reactivity will depend on the relative lifetime of the unstable arrangement of metal centre and non-reacting ligands, τ_M, compared with the lifetime of potential ligands in the second coordination sphere, τ_S.

When $\tau_M \gg \tau_S$, equilibrium between the second coordination sphere and solvent is established, the leaving ligand is solvated, and the ordered structure of the second coordination sphere is maintained. When $\tau_M \leqslant \tau_S$ the leaving ligand is present in the second coordination sphere during the reactions (it is only partly solvated) and the second coordination sphere has not relaxed to its preferred equilibrium structure. Current criteria involving linear free energy correlations and volumes of activation would correspond to the interpretation of this change in relative lifetimes as the result of increasingly associative behaviour, in agreement with the observed variation in effectiveness of water exchange vs. aquation of negatively charged ligands.

In conclusion, the kinetic parameters which have been used to deduce the degree of associative or dissociative character in the interchange classification of ligand substitution mechanisms for the reactions considered here could be assumed only indirectly to describe bonding differences in the transition state. The parameters may instead reflect the relative lifetimes and electrostatic interaction between the reactive intermediate or transition state of the metal and its depleted first coordination sphere and of the potentially reacting ligands in the second coordination sphere.

ACKNOWLEDGEMENT

Our thanks are due to Dr. E. Bang who supplied the data for Fig. 10 and to a referee for valuable comments.

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