

Water Ligand Exchange in Tetraammineiridium(III) Complexes. Kinetic *trans*-Effect in Octahedral Substitution Reactions

F. Galsbøl,^a L. Mønsted*^b and O. Mønsted^a

^aDepartment of Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 København Ø and ^bChemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

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Water ligand exchange in *trans*-tetraammineaqua- and in *trans*-tetraammineaquachloroiridium(III) has been investigated using an acidic 1 M perchlorate medium. Rate constants for the exchange of one water ligand and activation energies are: *trans*-[Ir(NH₃)₄(OH₂)₂]³⁺: $k(90^\circ\text{C}) = 1.73(7) \times 10^{-8} \text{ s}^{-1}$, $E_a = 165(4) \text{ kJ mol}^{-1}$; *trans*-[Ir(NH₃)₄(OH)(OH₂)]²⁺: $k(90^\circ\text{C}) = 7.6(7) \times 10^{-3} \text{ s}^{-1}$, $E_a = 96(3) \text{ kJ mol}^{-1}$, and *trans*-[Ir(NH₃)₄(OH₂)Cl]²⁺: $k(60^\circ\text{C}) = 5.30(8) \times 10^{-5} \text{ s}^{-1}$, $E_a = 113.0(13) \text{ kJ mol}^{-1}$. These data, in combination with literature data for water ligand exchange in pentaammineaquairidium(III), establish the kinetic *trans*-effect order, for a fixed set of *cis* ligands, as: OH₂ << NH₃ < Cl⁻ for substitution reactions at 25 °C at an iridium(III) centre. The variation in the kinetic *trans*-effect for iridium(III) as compared to rhodium(III) and chromium(III) for the same *trans*-ligand has been rationalized in terms of differences in ligand field stabilization energies.

The kinetic *trans*-effect for substitution reactions of octahedral metal complexes is considerably less well established than that for substitution in square-planar complexes, particularly in those of platinum(II). Unambiguous data are mainly available for rhodium(III) and chromium(III) complexes, and for both metal ions the kinetic *trans*-effect increases along the series OH₂ < NH₃ < Cl⁻ < Br⁻ < I⁻. This reactivity order is based upon data for aquation of coordinated chloride in aquachlororhodium(III) complexes,¹ for ligand substitution,^{2,3} including water ligand exchange⁴ in tetraamminerhodium(III) and pentaamminerhodium(III) complexes, and for water exchange in ammine-aquachromium(III)⁵⁻⁷ and pentaquahalogenochromium(III) complexes.^{8,9}

Kinetic *trans*-effect differences between rhodium(III) and chromium(III) have been rationalized using ligand field models,⁴ and such considerations should in principle be able to account for important features of substitution reactions of transition-metal ions in general. Data for water exchange in the *trans*-tetraammineaqua- and the *trans*-

tetraammineaquachloroiridium(III) ions are reported here in an attempt to obtain further evidence in support of the earlier hypothesis.

Results and discussion

Preparations. *trans*-Tetraammineaquachloroiridium(III) salts can be prepared by trifluoromethanesulfonate ligand aquation of the parent trifluoromethanesulfonate complex, which can be obtained by trifluoromethanesulfonate anation of *trans*-tetraamminedichloroiridium(III) chloride in neat trifluoromethanesulfonic acid. The spectral properties are shown in Fig. 1, and Table 1 gives a comparison of the acid dissociation constant with those of some other iridium(III) complexes.

Oxygen-18 enriched aquairidium(III) complexes are conveniently prepared by trifluoromethanesulfonate ligand aquation in oxygen-18 enriched water. This method has been used to prepare *trans*-[Ir(NH₃)₄(¹⁸OH₂)₂]³⁺ and *trans*-[Ir(NH₃)₄(¹⁸OH₂)Cl]²⁺, as previously described for the ox-

Table 1. Acid dissociation constants for some iridium(III) complexes in 1.0 M NaClO₄.

Complex	–log [K _a (25 °C) / M]	ΔH° / kJ mol ⁻¹	ΔS° / J K ⁻¹ mol ⁻¹	Ref.
<i>trans</i> -[Ir(NH ₃) ₄ (OH ₂) ₂] ³⁺	5.214(8)	44.6(12)	50(4)	This work
<i>trans</i> -[Ir(NH ₃) ₄ (OH)(OH ₂)] ²⁺	8.052(9)	46.1(13)	0(5)	This work
<i>trans</i> -[Ir(NH ₃) ₄ (OH ₂)Cl] ²⁺	6.532(6)	43.4(9)	20(3)	This work
[Ir(NH ₃) ₅ (OH ₂)] ³⁺	6.716(7)	46.8(12)	28(4)	10
<i>cis</i> -[Ir(NH ₃) ₄ (OH ₂) ₂] ³⁺	6.265(7)	44.8(12)	30(4)	17
<i>cis</i> -[Ir(NH ₃) ₄ (OH)(OH ₂)] ²⁺	8.088(9)	46.6(13)	1(5)	17

* To whom correspondence should be addressed.

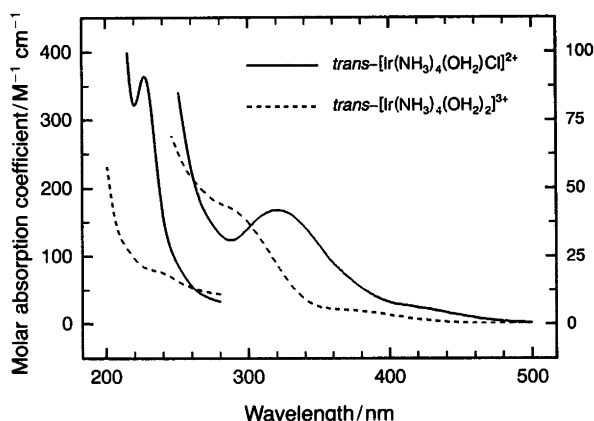


Fig. 1. UV-VIS spectra of $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+}$ and of $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$ in 0.1 M HClO_4 .

ogen-18 labelled ammineaquabis(1,2-ethanediamine)rhodium(III) complexes.¹¹

Water ligand exchange kinetics. The water ligand exchange as function of time was monitored mass-spectrometrically in the solvent water after separation from the dissolved salts. For both complexes the relative increase in oxygen-18 in the solvent water, δ_{exp} , was found accurately to follow a theoretical expression of the form expected for exchange of one type of water ligands, i.e. eqn. (1), where t is the time,

$$\delta_{\text{exp}} \approx \delta_{\text{calc}} = \delta_0 + \delta_c [\exp(-kt) - 1] \quad (1)$$

δ_0 and δ_c are parameters, and k is the rate constant for exchange of one water ligand.⁵

For *trans*-tetraamminediaquairidium(III) the observed first-order rate constants were found to depend on the hydrogen ion concentration according to eqn. (2), in agree-

$$k_{\text{obs}} \approx k_{\text{calc}} = k_0 + k_1 K_a / [\text{H}^+] \quad (2)$$

ment with reactivity contributions from both the tetraamminediaqua- and the tetraammineaquahydroxoiridium(III)

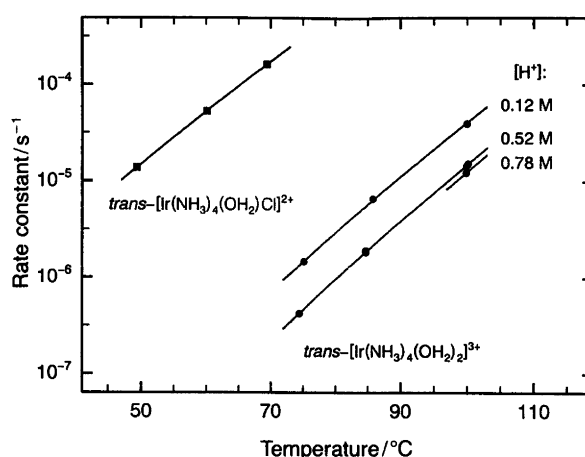


Fig. 2. Dependence on temperature and hydrogen-ion concentration of water ligand exchange in $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+}$ and in $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$ in 1.0 M $(\text{H,Na})\text{ClO}_4$. The curves are calculated from the parameters in Table 2.

complexes. k_0 is the rate constant for exchange of one water ligand in $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$, k_1 is the rate constant for exchange of one water ligand in $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH})(\text{OH}_2)]^{2+}$, and K_a is the acid dissociation constant for $\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$. A summary of rate constants as a function of temperature and hydrogen ion concentrations is given in Fig. 2, and rate constants and activation energies are given in Table 2.

Kinetic trans-effect. Rate constants at 25°C and activation parameters derived from the data in Tables 1 and 2 are given in Table 3, together with literature data for water exchange in $[\text{Ir}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$.¹² The interpretation of these data is free from some of the ambiguities which arise in an interpretation of kinetic data with non-zero changes in free energies of reaction, and they directly reveal a very large kinetic *trans*-effect, which is seen to follow inequality (3). This kinetic *trans*-effect order is the



Table 2. Rate constants and activation energies for the exchange of one water ligand in some *trans*-iridium(III) complexes.

Complex	$T/^\circ\text{C}$	$k_0/10^{-6} \text{ s}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$k_1 K_a/10^{-6} \text{ s}^{-1} \text{ M}^{-1}$	$E_a/\text{kJ mol}^{-1}$
$\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	90.0	1.73(7)	165(4)	1.16(3)	141(2)
$\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+}$	60.0	53.0(8)	113.0(13)	—	—

Table 3. Kinetic parameters for the exchange of one water ligand in some iridium(III) complexes.

Complex	$k(25^\circ\text{C})/10^{-7} \text{ s}^{-1}$	$\Delta G^\ddagger(25^\circ\text{C})/\text{kJ mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	Ref.
$[\text{Ir}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$	0.64(4)	114.1(18)	117.6(13)	11(4)	12
$\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)_2]^{3+}$	0.000 11(3)	136(6)	162(4)	90(10)	This work
$\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]^{2+}$	4.4(5)	109.3(15)	110.2(13)	3(4)	This work
$\text{trans-}[\text{Ir}(\text{NH}_3)_4(\text{OH})(\text{OH}_2)]^{2+}$	72(11)	102(4)	93(3)	-31(7)	This work

same as that for both rhodium(III) and chromium(III). Empirically, however, the kinetic *trans*-effect for iridium(III) is seen to be somewhat larger than for rhodium(III) and significantly larger than that for chromium(III).

Ligand field considerations. The order of ligands in inequality (3) cannot be correlated with the order of empirical values for σ - and π -bonding in chromium(III),¹³ rhodium(III)¹⁴ or iridium(III), but follows the ligand order in the nephelauxetic series. The significantly larger effect for the low-spin d^6 configuration of rhodium(III) and iridium(III) than for the d^3 configuration of chromium(III) suggests, however, that ligand field effects are important for the metal ion dependent part of the kinetic *trans*-effect.

Application of ligand field models to kinetic problems requires consideration of both the ground state and the transition state, and angular overlap model calculations show that the contributions to the energy of activation from the ligand field of the *trans*-ligand is accurately proportional to the difference between the Δ -values of this ligand in the ground state and in the transition state, with proportionally factors 1/5 for chromium(III) and 2/5 for rhodium(III) and iridium(III).⁴

With the assumption that the relative change in the Δ -parameter of the *trans*-ligand when going from the ground state to the transition state is the same, and using the approximate empirical separation of Δ into a ligand, T, and a metal, M, dependent part¹⁵ [approximation (4)], it is

$$\Delta_{T[M]} \approx f_T g_M \quad (4)$$

readily verified that changes in free energies of activation for a series of reactions in which only the *trans*-ligand is varied are proportional according to approximations (5) and (6).

$$\delta(\Delta G^*_{Cr(III)}) \approx (g_{Cr(III)}/2g_{Ir(III)}) \cdot \delta(\Delta G^*_{Ir(III)}) \quad (5)$$

$$\delta(\Delta G^*_{Rh(III)}) \approx (g_{Rh(III)}/g_{Ir(III)}) \cdot \delta(\Delta G^*_{Ir(III)}) \quad (6)$$

The validity of these approximations is tested in Fig. 3 and they are seen to describe rather well the metal ion dependent differences in kinetic *trans*-effect between the present chromium(III), rhodium(III) and iridium(III) complexes.

Mechanism of ligand substitution. The mechanism of ligand substitution in octahedral metal complexes has been much debated, and, particularly for the substitution reactions in the pentaamminechromium(III) series of complexes, different criteria have been used differently to classify these substitution reactions. The importance of the second coordination sphere was recently stressed, and it was suggested that the commonly used mechanistic classification labels could reflect the degree of second-sphere re-equilibration during the ligand interchange process,¹⁶ the 'associative'

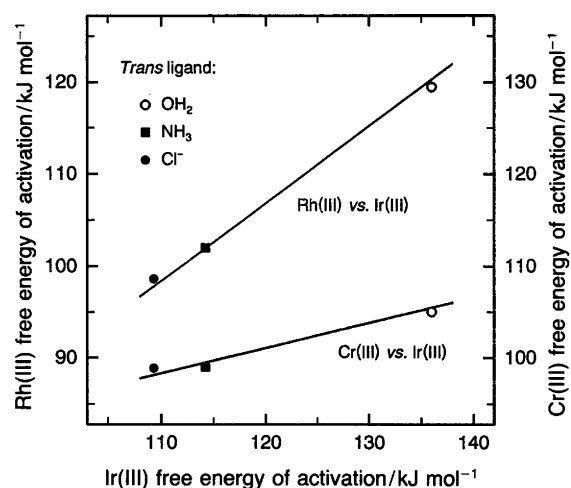


Fig. 3. Correlation between kinetic *trans*-effect of water, ammonia and chloride in chromium(III), rhodium(III) and iridium(III) complexes. The straight lines are drawn with slopes calculated from the non-kinetic g -parameters of Ref. 15: $g[Cr(III)] \approx 208 \text{ kJ mol}^{-1}$ ($1.74 \mu\text{m}^{-1}$), $g[Rh(III)] \approx 323 \text{ kJ mol}^{-1}$ ($2.70 \mu\text{m}^{-1}$) and $g[Ir(III)] \approx 383 \text{ kJ mol}^{-1}$ ($3.20 \mu\text{m}^{-1}$). The kinetic data are from Table 3 and Ref. 4.

labelling being indicative of little re-equilibration, and the 'dissociative' labelling being indicative of significant or complete re-equilibration.

Formation of the transition state will be accompanied by an increasing bond length between the metal centre and the substituted ligand. Assuming a bonding pattern in the transition state that is similar to that in the ground-state structures, this significant bond stretching will occur concomitant with a bond strengthening to the ligand in a *trans*-position to the leaving ligand. This would be expected to result in a larger field stabilization contribution from the *trans*-ligand in the transition state than in the ground state. Interpreted this way, the kinetic *trans*-effect reflects relative differences in bond strengthening to the *trans*-ligand in the transition state. Second-sphere solvation is clearly of importance in this context, and the present interpretation therefore provides a rationale for the empirical correlation between larger kinetic *trans*-effects of poorly solvated *trans*-ligands.

Experimental

Caution. The perchlorate salt described here is potentially explosive and should be handled accordingly.

Chemicals. $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ was obtained from Johnson Matthey Chemicals, ^{18}O -enriched water from Alfa Products and trifluoromethanesulfonic acid from the 3M Company. Other commercial chemicals were of analytical grade. *trans*- $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ ¹⁰ and *trans*- $[\text{Ir}(\text{NH}_3)_4(\text{OH})(\text{OH}_2)](\text{ClO}_4)_2$ ¹⁷ were prepared by literature methods. The trifluoromethanesulfonate form of the Bio-Rad AG 1-X8 cation exchanger was prepared from the commercially available chloride form by treatment with aqueous sodium

carbonate, followed by adding an excess of aqueous trifluoromethanesulfonic acid and thorough washing with water.

Preparations

1. *trans*-[Ir(NH₃)₄Cl(OSO₂CF₃)]CF₃SO₃. 1.00 g of *trans*-[Ir(NH₃)₄Cl₂]Cl · H₂O (2.60 mmol) was dissolved in 5 ml of anhydrous CF₃SO₃H in a 25 ml flask equipped with a stirring magnet and under a stream of nitrogen. The flask was lowered into an oil bath preheated to 110 °C and flushed with a stream of nitrogen for 1 h. Heating and stirring were continued for a further 23 h, after which the solution was again flushed with nitrogen for 15 min, and then allowed to cool in ice under nitrogen. 20 ml of dry diethyl ether were next added dropwise to the rapidly stirred solution. This precipitated the complex, which was filtered off under nitrogen and washed four times with diethyl ether. The solid was treated for 30 min with 20 ml of boiling chloroform, cooled in ice and then filtered under nitrogen, washed with chloroform and left to dry under nitrogen. Yield: 1.4 g (91 %) of *trans*-[Ir(NH₃)₄Cl(OSO₂CF₃)]CF₃SO₃. Analyses: C, H, N, Cl and S.

2. *trans*-[Ir(NH₃)₄(OH₂)Cl](CF₃SO₃)₂. 1.30 g (2.19 mmol) of *trans*-[Ir(NH₃)₄Cl(OSO₂CF₃)]CF₃SO₃ were dissolved in 1.5 ml of water by heating to boiling. The solution was filtered while hot and the filter was washed twice with 0.5 ml of water. 1 ml of CF₃SO₃H was added to the combined filtrate and washings, which resulted in a copious precipitate. The mixture was heated until the precipitate dissolved and the resulting solution was left to crystallize, first at room temperature and then overnight at 5 °C. The crystals were filtered off and washed twice with 0.5 ml of ice-cold abs. ethanol, then with diethyl ether, and were left to dry in air. Yield: 0.9 g (67 %) of yellow *trans*-[Ir(NH₃)₄(OH₂)Cl](CF₃SO₃)₂. Analyses: C, H, N and Cl.

3. *trans*-[Ir(NH₃)₄(OH₂)Cl](ClO₄)₂. 1.40 g (2.36 mmol) of *trans*-[Ir(NH₃)₄Cl(OSO₂CF₃)]CF₃SO₃ were dissolved in 1.5 ml of water by heating to boiling as described in preparation 2. 0.5 ml of 70 % HClO₄ was added dropwise to the filtrate, which was then heated until the precipitate dissolved. The solution was left at room temperature for crystallization, and then cooled in ice. The crystals were filtered off and washed, twice with 1 ml of ethanol, then with diethyl ether, and were left to dry in air. Yield: 1.0 g (83 %). The product could be recrystallized from hot water by the addition of 70 % HClO₄ as described above. Yield: 0.9 g (75 %) of yellow *trans*-[Ir(NH₃)₄(OH₂)Cl](ClO₄)₂. Analyses: C, H, N and Cl.

4. *trans*-[Ir(NH₃)₄(OSO₂CF₃)₂]CF₃SO₃. 1.00 g (2.02 mmol) of *trans*-[Ir(NH₃)₄(OH)(OH₂)](ClO₄)₂ was dissolved in 25 ml of water and the solution applied to a 13×1 cm column of Bio-Rad AG 1-X8 anion exchanger on the CF₃SO₃⁻-form, which was then washed with 10 ml of water. The eluate was evaporated to dryness in vacuum, and the residue treated with 5 ml of anhydrous CF₃SO₃H for 30 min at ca. 100–120 °C. The complex was precipitated by the addition of 40 ml of dry diethyl ether and isolated as described in preparation 1. The solid was boiled in 20 ml of

chloroform for 30 min, filtered off under nitrogen, and dried in a stream of nitrogen. Yield: 1.4 g (98 %) of *trans*-[Ir(NH₃)₄(OSO₂CF₃)₂]CF₃SO₃. Analyses: C, H and N.

Preparation of oxygen-18 enriched aquairidium(III) complexes. About 150 mg *trans*-[Ir(NH₃)₄(OSO₂CF₃)₂]CF₃SO₃ or about 350 mg *trans*-[Ir(NH₃)₄Cl(OSO₂CF₃)]CF₃SO₃ were dissolved in 1 ml ¹⁸OH₂ adjusted to [H⁺] ≈ 0.01 M with *p*-toluenesulfonic acid, and kept at 70 °C overnight. The solution was freeze-dried to recover the excess of water, and the solid was then dissolved in 5 ml water, [H⁺] ≈ 0.01 M, and purified on a Sephadex SP-C-25 ion-exchange column as described previously.¹¹ In order to be able to follow the elution on the column in subdued light, [Cr(NH₃)(OH₂)₅]³⁺ or [Cr(NH₃)₅Br]²⁺ was added to the solutions of *trans*-[Ir(NH₃)₄(OH₂)₂]³⁺ and *trans*-[Ir(NH₃)₄(OH₂)Cl]²⁺, respectively.

Methods. Determination of acidity constants,¹⁸ kinetic measurements, mass spectrometric measurements, spectrophotometric measurements, methods of analysis and methods of calculation have all been described previously.⁵

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