Formation and Cleavage of Hydroxo-Bridged Dinuclear Iridium(III) Ammine and 1,2-Ethanediamine Complexes

Frode Galsbøl,[a] Karen Kaas,[b] Bente Nielsen[b] and Johan Springborg[†,b]

[a] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark and [b] Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsenvej 40, DK-1871 Frederiksberg C, Denmark

Galsbøl, F., Kaas, K., Nielsen, B. and Springborg, J., 1995. Formation and Cleavage of Hydroxo-Bridged Dinuclear Iridium(III) Ammine and 1,2-Ethanediamine Complexes. – Acta Chem. Scand. 49: 44–52 © Acta Chemica Scandinavica 1995.

The equilibration reaction between the mononuclear species cis-Ir(NH$_3$)$_4$-(H$_2$O)$_2$$^{3+}$ (and its deprotonated forms) and the dinuclear species cis,cis-(H$_2$O)(NH$_3$)$_4$Ir(OH)Ir(NH$_3$)$_4$(OH$_2$)$^{5+}$ (and deprotonated forms) and (NH$_3$)$_4$Ir(OH)$_2$Ir(NH$_3$)$_4$$^{4+}$ has been studied at 60–100°C in 1 M (Na,H)ClO$_4$ with [H$^+$] = 10^{-7} – 1.0 M using spectrophotometry and IE-HPLC. The corresponding 1,2-ethanediamine complexes were also studied. The results are interpreted in terms of the equilibria between the mononuclear and dinuclear (mono- and dihydroxo-bridged) species, and in the case of the 1,2-ethanediamine system also including $meso$ (Δ,Λ) as well as $racemic$ (Δ,Δ/Λ,Λ) dinuclear species. Data for the equilibria between the dinuclear species have been published previously, and in this study the thermodynamic (K_3/K_{a3}, K_4, K_5 and K_6) and kinetic (k_3/K_{a3}, k_4 and k_5 and k_{-3}, k_{-4} and k_{-5}) parameters for the equilibria between mononuclear and dinuclear monohydroxo-bridged species are given.

Hydrolysis of aqua-metal ions to form hydroxo-bridged polynuclear complexes has been reported for most transition metals and is of significance in the aqueous chemistry of such ions.[1-3] These reactions are of relevance to geological processes (properties and formation of oxides) and biology (many metalloproteins contain hydroxo-bridged dinuclear metal centres). An important reaction in the initial stage of these polymerization reactions is the equilibrium between the mono- and dihydroxo-bridged species exemplified in the upper part of Scheme 1. Equilibria between mono- and dihydroxo-bridged species of chromium(III), rhodium(III) and iridium(III) have been studied extensively during the last two decades, and the mechanistic aspects of this type of reaction are now fairly well understood.[1,3] Equilibria between these monohydroxo-bridged species and their parent mononuclear species are less studied.[1] Recently detailed kinetic studies of the rhodium(III) systems with ammonia and 1,2-ethanediamine (Δ,Λ-isomers) have been reported,[4-6] and we report here our results for the corresponding ammine and amine complexes with iridium(III).

Experimental

Materials and instruments. All coordination compounds were prepared as reported previously.[7-9] All reagents

were of analytical grade, and distilled water was used for all measurements. A Perkin Elmer diode array spectrophotometer was used for spectral measurements. The pH measurements were made using Radiometer equipment as reported previously.[10] The ion-exchange high-performance liquid chromatography (IE-HPLC, Waters equipment) was performed as described previously.[5] In all experiments the eluent was 0.19–0.22 M Na$_2$SO$_4$.

Determination of acid dissociation constants. The concentration acid dissociation constants of cis-Ir(en)$_2$(H$_2$O)$_2$$^{3+}$ were determined by titration of a solution of cis-[Ir(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ in an excess of perchloric acid with sodium hydroxide at an ionic strength of 1 M kept constant with sodium perchlorate. The determinations were made at 44.9°C and gave the values pK_{a1} = 5.604(28) and pK_{a2} = 7.533(10). Using these values, together with previously published[7] values at 25°C, the Δ$H°$ and Δ$S°$ values were calculated (Table 1).

Determination of the dimerization constants. Equilibrium solutions of the ammine complexes were obtained by heating solutions of either cis-[Ir(NH$_3$)$_4$(H$_2$O)(OH)](ClO$_4$)$_2$·H$_2$O or [(NH$_3$)$_4$Ir(OH)$_2$Ir(NH$_3$)$_4$]-(ClO$_4$)$_4$·2H$_2$O in 1 M NaClO$_4$, kept in glass ampoules, at 65.0, 85.0 and 100.0°C for 180, 25–50 and 7–8 days, respectively. Here and in the following the temperatures were normally kept constant within ±0.05°C, but in a few cases the errors were ±0.1°C. The ampoules were

---

† To whom correspondence should be addressed.

Table 1. Acid dissociation constants for mononuclear (K_a^m) and dinuclear (K_a^d) ammine and 1,2-ethanediamine iridium(III) species at 25 °C in NaClO$_4$[a]

Constants	Value	ΔH° /kJ mol^{-1}	ΔS° /J mol^{-1}K^{-1}	Ref.
pK_{a1}^m (NH$_3$)	6.265(7)	44.8(12)	30(4)	8
(en)	6.145(8)	49.4(27)	48(9)	This work[b]
pK_{a2}^m (NH$_3$)	8.088(9)	46.6(12)	1(4)	8
(en)	8.001(11)	42.7(13)	−10(4)	This work[b]
pK_{a1}^d (NH$_3$)	3.115(4)	42.5(7)	83(2)	8
(en)	1.91(2)	10.8(67)	−1(22)	9
pK_{a2}^d (NH$_3$)	9.012(8)	58.9(12)	25(4)	8
(en)	9.04(3)	53.3(50)	6(14)	9

[a] See also Scheme 1. For the 1,2-ethanediamine species pK_a^d are for the Δ,Λ-isomers. Here and in the following standard deviations are given in parenthesis in units of the last decimal. [b] ΔH° and ΔS° have been calculated from previously published values of pK_a^m at 25 °C (Ref. 7) and values of pK_a^m at 45 °C determined in this study.

frozen and kept at −18 °C until they were used for the IE-HPLC measurements. The IE-HPLC measurements (Fig. 1) were made at 25 °C. The frozen samples were melted and then kept at 0 °C for as short a time as possible before the measurements, in order to avoid re-equilibration at 25 °C between the monohydroxo- and dihydroxo-bridged species. The equilibrium solutions of the 1,2-ethanediamine complexes were made similarly starting with *cis*-[Ir(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ or Δ,Λ-[(en)$_2$Ir(OH)$_2$Ir(en)$_2$](ClO$_4$)$_4$ and heated at 65.0, 85.0 and 100.0 °C for 180, 25–29 and 3–4 days, respectively.

The concentrations of the mononuclear species and of the monohydroxo- and dihydroxo-bridged species were calculated from the relative peak areas as described previously.[5] The molar absorption coefficients of the unidentified mono- and dinuclear species were assumed to be equal to those of the known mono- and dinuclear species, e.g. for the ammine system equal to those of

cis-[Ir(NH$_3$)$_4$(H$_2$O)(OH)]$^{2+}$ and [(NH$_3$)$_4$Ir(OH)$_2$-Ir(NH$_3$)$_4$]$^{4+}$, respectively. Likewise, the molar absorption coefficients of *racemic* complexes with 1,2-ethanediamine were assumed to be equal to those of the corresponding *meso* isomers. It is noted that even a relatively large error for these estimated molar absorption coefficients will only cause a minor error in the estimated values for K_5 and no error in the estimates for K_1. For example, for the ammine system it is calculated that if the estimated molar absorption coefficients are increased by 50%, then the values for K_5 will increase by 8–14%. Furthermore, the observation that the values for K_5 are nearly the same for different C_{Ir} values suggests that the present estimates for the molar absorption coefficients are reasonable. The equilibrium constants K_1 and K_5 were then calculated as described under Results. (See also Tables 2–6.)

Kinetic measurements. Reactant solutions were made by dissolving either [(NH$_3$)$_4$Ir(OH)$_2$Ir(NH$_3$)$_4$](ClO)$_4$·H$_2$O or Δ,Λ-[(en)$_2$Ir(OH)$_2$Ir(en)$_2$](ClO$_4$)$_4$ in 1 M (Na,H)ClO$_4$ $(C_{Ir} = 1.4 \times 10^{-5} - 4 \times 10^{-4}$ M). Under the conditions used, the reaction to mononuclear species has half-lives from 1 h to 108 days for the ammine system, and for the amine system the half-lives are from 1 h to 80 days. Some kinetic experiments were based upon repetitive scanning of the absorption spectra, but most experiments were made using aliquots of the solution, kept separately in glass ampoules in the dark. Pseudo-first-order rate constants, k_{obs}, were calculated using non-linear regression analysis. In each kinetic run the rate constants were calculated on the basis of absorbancies measured at 161 different wavelengths in the region 240–400 nm.

The hydrogen ion concentration changed slightly during a kinetic experiment. The hydrogen ion concentration in the original equilibrated solutions of dinuclear species, [H$^+$]$_0$, and in the final solutions of mononuclear species, [H$^+$]$_{eq}$, were calculated from the solution stoichiometry using the relevant thermodynamic parameters given in Tables 1 and 2. For solutions with [H$^+$]$_0 > 10^{-2}$ M the variations of the hydrogen ion concentration were <4%.

Table 2. Thermodynamic data for the equilibrium:[a] L$_4$M(OH)$_2$ML$_4$$^{4+}$ + H$_2$O $\overset{K}{\rightleftharpoons}$ (H$_2$O)L$_4$M(OH)ML$_4$(OH)$^{4+}$.

M	L	Configuration	K_1	ΔH° /kJ mol^{-1}	ΔS° /J^{-1}K^{-1}	Ref.
Cr(III)	(NH$_3$)$_4$		0.32(1)	6(4)	11(14)	10
Rh(III)	(NH$_3$)$_4$		3.03(4)	2(1)	15(4)	11
Ir(III)	(NH$_3$)$_4$		3.3(6)	−2(3)	2(9)	8
—	—		3.4(1)	−4(5)	−2(13)	This work[b]
—	—		3.4(4)	−4(2)	−1(5)	
Cr(III)	(en)$_2$	Δ,Λ	0.75(2)	−3(1)	−13(3)	10, 12
Cr(III)	(en)$_2$	Δ,Δ/Λ,Λ	0.22(3)	−2(4)	−19(13)	10, 13
Rh(III)	(en)$_2$	Δ,Λ	11.2(5)	−14(3)	−28(8)	14
Rh(III)	(en)$_2$	Δ,Δ/Λ,Λ	1.89(4)	−9(1)	−23(4)	5
Ir(III)	(en)$_2$	Δ,Λ	5.7(8)	−2(5)	10(15)	9
Ir(III)	(en)$_2$	Δ,Δ/Λ,Λ	0.99(17)	−4(3)	−13(7)	This work

[a] 1 M NaClO$_4$, 25 °C. [b] Calculated from the values of K_1(65–100 °C) obtained by IE-HPLC in this study combined with our previous[4] values of K_1(35–100 °C) determined by spectrophotometry.

At lower [H$^+$] larger variations were calculated (6% for [H$^+$]$_0$ = 0.005 M and C_{Ir} = 4 × 10^{-4} M), but in this region the observed dependence of k_{obs} on [H$^+$] is small. It is therefore concluded that the variations in [H$^+$] during a single experiment can be ignored, and that pseudo-first-order conditions can be assumed. The value [H$^+$] = 1/2([H$^+$]$_0$ + [H$^+$]$_{eq}$) was then used in the following calculations.

For solutions in pure 1 M NaClO$_4$ it was found by glass-electrode measurements that pH values in the product solutions were in the region 6–7. In this pH region the observed rate has practically no dependence on the pH, but as mentioned under Results there is a considerable formation of by-products. In the following calculations of the kinetic data the theoretical values for the final concentrations of the hydrogen ions were used and were obtained using pH = $^1/_2$(pK_{a1} + pK_{a2}), where pK_{a1} and pK_{a2} are the acid dissociation constants of the mononuclear diaqua species (Table 1).

The activation parameters were fitted by minimizing the sum of [ln(k_{obs}) – ln(k_{calc})]^2, the values of k_{calc} being defined by eqn. (1) and k_r = ($k_B T/h$)exp(Δ$S^{\ddagger}$/R – Δ$H^{\ddagger}$/RT).

Results

Stoichiometry and determination of dimerization constants. The (NH$_3$)$_4$Ir(OH)$_2$Ir(NH$_3$)$_4{}^{4+}$ ion undergoes bridge cleavage in neutral and acidic solution to give the mononuclear species *cis*-Ir(NH$_3$)$_4$(H$_2$O)$_2{}^{3+}$ and its deprotonated forms. The bridge cleavage occurs in two kinetically well separated steps. Equilibration between the monohydroxy- and dihydroxo-bridged species in acidic and neutral solution has previously[8,9] been shown to involve the equilibria shown in the upper part of Scheme 1. In the present work the equilibria between the mononuclear and dinuclear species have been studied (lower part of Scheme 1). In acidic solution the equilibria are shifted almost completely to the mononuclear species (see also below), and a determination of the equilibrium constants is difficult in this region. Equilibrium studies were therefore restricted to almost neutral solutions, which for large iridium(III) concentrations contain significant amounts of both mononuclear and dinuclear species.

The *meso* (Δ,Λ) 1,2-ethanediamine complexes react in the same way as the ammine complexes, but now additional equilibria involving the formation of the corresponding *racemic* (Δ,Δ and Λ,Λ) species has also to be considered as shown in Scheme 2. While the Δ,Λ-isomers have been isolated as salts and characterized by X-ray structure analysis,[9] the Δ,Δ- and Λ,Λ-isomers have not been isolated, nor characterized previously.

For both the ammine and the amine system the equilibrium solutions were made by starting with either mono- or dinuclear species, and were analyzed by ion-exchange high-performance liquid chromatography (IE-HPLC). The following observations show that equilibrium be-
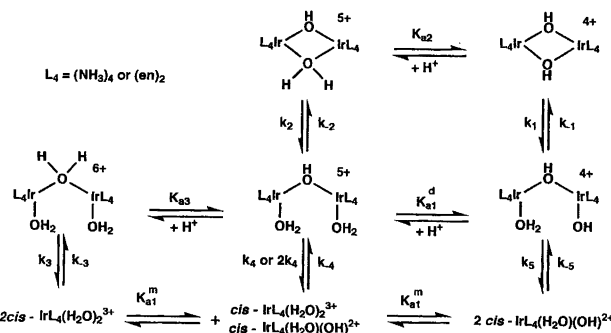
Scheme 1. Reaction scheme for the equilibrium between mononuclear and dinuclear species. L$_4$ = (NH$_3$)$_4$ or L$_4$ = (en)$_2$ (Δ,Λ-isomers). In the ammine system k_4 is the rate constant for cleavage to *cis*-Ir(NH$_3$)$_4$(H$_2$O)$_2{}^{3+}$ and *cis*-Ir(NH$_3$)$_4$(H$_2$O)(OH)$^{2+}$. In the 1,2-ethanediamine system k_4 corresponds either to formation of Δ-*cis*-Ir(en)$_2$(H$_2$O)$_2{}^{3+}$ and Λ-*cis*-Ir(en)$_2$(H$_2$O)(OH)$^{2+}$ or to the formation of Λ-*cis*-Ir(en)$_2$(H$_2$O)$_2{}^{3+}$ and Δ-*cis*-Ir(en)$_2$(H$_2$O)(OH)$^{2+}$. Analogously k_{-4} corresponds to the reactions of two different pairs of mononuclear species. See also the Appendix.
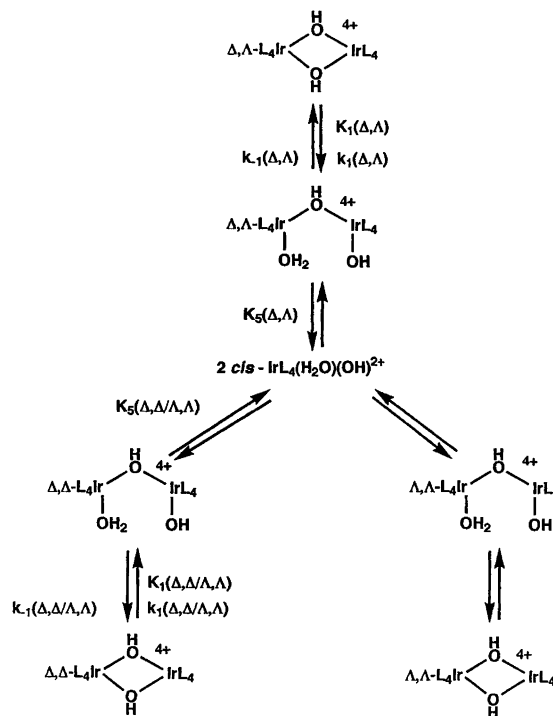
Scheme 2. Equilibria between *meso* (Δ,Λ) and *racemic* (Δ,Δ/Λ,Λ) dinuclear species and the parent mononuclear species. The scheme has been simplified in the sense that 2 *cis*-Ir(en)$_2$(H$_2$O)(OH)$^{2+}$ refers to the following three combinations of isomers Δ+Λ, Δ+Δ and Λ+Λ. It is noted that K$_1$(Δ,Δ/Λ,Λ) and K$_5$(Δ,Δ/Λ,Λ) refer to either the Δ,Δ (as shown at left) or the Λ,Λ isomers.

tween the species in Scheme 1 (and also Scheme 2 for the 1,2-ethanediamine system) had been achieved. Identical chromatograms were obtained for solutions initially containing mononuclear or dinuclear species and with the same total concentration of iridium(III). Heating of so-

lutions for two different times gave within the error the same equilibrium constants. The same equilibrium constants were obtained when C_{Ir} was varied. However, the experiments were complicated by the formation of additional by-products as shown in Figs. 1 and 2.

The peaks of the chromatograms were identified, when possible, by comparing the elution rates, and the UV spectra with those of the known mono- and dinuclear species. The chromatogram of the ammine equilibrium mixture shown in Fig. 1 has six peaks, of which the three correspond to cis-Ir$(NH_3)_4(H_2O)_2{}^{3+}$ (and its deprotonated forms) and the known dinuclear species cis,cis-$(H_2O)(NH_3)_4Ir(OH)Ir(NH_3)_4(OH)^{4+}$ and $(NH_3)_4Ir(OH)_2Ir(NH_3)_4{}^{4+}$. The remaining three peaks were not identified, but from the elution rates it is assumed that the first two are due to monomeric species, while the last is due to dinuclear species.

The actual concentrations of the species cis-Ir$(NH_3)_4(H_2O)(OH)^{2+}$ were calculated from the sum of the concentrations of mononuclear species determined above using the known acid dissociation constants (Table 1). The concentration of the aquahydroxo species constitute ca. 80% of the total concentration of mononuclear species. The acid dissociation constants of cis,cis-$(H_2O)(NH_3)_4Ir(OH)Ir(NH_3)_4(OH_2)^{4+}$ are given in Table 1; it is seen that the dominant species in the equilibrium solutions will be the aquahydroxo form, and corrections due to the presence of protonated and deprotonated forms are not necessary. The constants $K_1 = k_1/k_{-1}$ and $K_5 = k_5/k_{-5}$, defined as shown in Scheme 1, and their enthalpic and entropic parameters were then calculated (Tables 3 and 5). It is satisfactory to note that the value for K_1 is nearly identical to the value obtained by spectrophotometry (Table 2) which we reported recently.
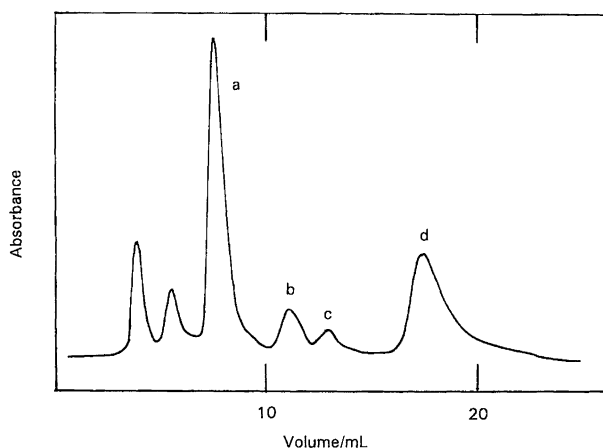
Table 3. Thermodynamic data for the ammine system in 1 M $NaClO_4$ obtained by IE-HPLC.

$T/°C$	C_{Ir}/M	Time /days	K_1 (obs)	K_1 (calc)[b]	K_5(obs) /M^{-1}	K_5(calc)[c] /M^{-1}
65.0	0.009[a]	180	2.5	2.9	0.0102	0.0106
65.0	0.04[a]	180	2.9	–	0.0119	–
85.0	0.01	25	3.2	2.7	0.0086	0.0104
85.0	0.01	50	3.0	–	0.0106	–
100.0	0.01	7	2.3	2.5	0.0115	0.0103
100.0	0.01[a]	8	2.2	–	0.0104	–

[a] The equilibrium solutions in these experiments were made by starting with monomer. In all the other experiments the solutions were made starting with the dinuclear complex. [b] Calculated using the values of $\Delta H°$ and $\Delta S°$ given in Table 2. [c] Calculated using the values of $\Delta H°$ and $\Delta S°$ given in Table 5.

A chromatogram of the equilibrium mixture of the 1,2-ethanediamine species is shown in Fig. 2, and it shows that, in addition to the known meso (Δ,Λ) isomers of the dinuclear species, the racemic $(\Delta,\Delta/\Lambda,\Lambda)$ species are also formed. The identification of these new species has been based upon the expected similarity in the elution rates and of the absorption spectra of different isomers of the same cation and by comparison with the results for the corresponding rhodium(III) system.[5] It is noted that only one peak occurs for the two isomers $(\Delta,\Lambda$ and $\Delta,\Delta/\Lambda,\Lambda)$ of the dihydroxo-bridged species, while the two mono-hydroxo-bridged isomers $(\Delta,\Lambda$ and $\Delta,\Delta/\Lambda,\Lambda)$ are well separated (Fig. 2). A similar poor resolution of the two dihydroxo-bridged isomers, and good separation of the two monohydroxo-bridged isomers was also observed in the corresponding rhodium(III) study.[5] The remaining
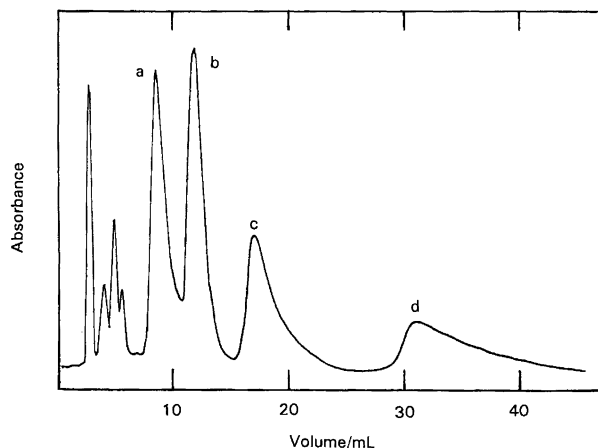

Fig. 1. IE-HPLC chromatogram (25°C, 270 nm) for a solution of $[(NH_3)_4Ir(OH)_2Ir(NH_3)_4](ClO_4)_4$ ($C_{Ir}=0.01$ M) in 1 M $NaClO_4$ heated for 605 h at 85°C. Peaks (a)–(d) have been assigned as follows: (a) cis-Ir$(NH_3)_4(H_2O)(OH)^{2+}$; (b) $(NH_3)_4Ir(OH)_2Ir(NH_3)_4{}^{4+}$; (c) unidentified dinuclear species; (d) cis,cis-$(H_2O)(NH_3)_4Ir(OH)Ir(NH_3)_4(OH)^{4+}$. The first two peaks were not identified but are probably due to mononuclear species.

Fig. 2. IE-HPLC chromatogram (25°C, 270 mm) for a solution of Δ,Λ-$[(en)_2Ir(OH)_2Ir(en)_2](ClO_4)_4$ ($C_{Ir}=0.046$ M) in 1 M $NaClO_4$ heated for 72 h at 100°C. Peaks (a)–(d) have been assigned as follows: (a) cis-Ir$(en)_2(H_2O)(OH)^{2+}$; (b) Δ,Λ-$(en)_2Ir(OH)_2Ir(en)_2{}^{4+}$ and $\Delta,\Delta/\Lambda,\Lambda$-$(en)_2Ir(OH)_2Ir(en)_2{}^{4+}$; (c) Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4+}$; (d) $\Delta,\Delta/\Lambda,\Lambda$-$(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4+}$. The first four peaks were not identified but are probably due to mononuclear species.

47

Table 4. Thermodynamic data for the 1,2-ethanediamine system in 1 M $NaClO_4$ obtained by IE-HPLC.

T /°C	C_{Ir} /M	Time /days	$K_1(\Delta,\Delta)$(obs) /M^{-1}	$K_1(\Delta,\Delta)$(calc)[b] /M^{-1}	$K_5(\Delta,\Delta)$(obs) /M^{-1}	$K_5(\Delta,\Lambda)$(calc)[c] /M^{-1}	$K_5(\Delta,\Delta)$(obs) /M^{-1}	$K_5(\Delta,\Lambda)$(calc)[d] /M^{-1}
65.0	0.04[a]	180	0.78	0.82	0.0034	0.0033	0.0103	0.0095
65.0	0.04[a]	180	0.80	–	0.0030	–	0.0089	–
65.0	0.04	180	0.88	–	0.0035	–	0.0091	–
85.0	0.05	25	0.69	0.76	0.0046	0.0053	0.0130	0.0131
85.0	0.05	29	0.81	–	0.0070	–	0.0159	–
100.0	0.01	3	0.80	0.72	0.0065	0.0073	0.0139	0.0164
100.0	0.05[a]	4	0.64	–	0.0073	–	0.0169	–

[a] The equilibrium solutions in these experiments were made by starting with monomer. In all the other experiments the solutions were made starting with the dinuclear complex. [b-d] Calculated using the values of $\Delta H°$ and $\Delta S°$ given in [b] Table 2, [c] Table 5 and [d] Table 6.

four peaks were not identified, but are all assumed to be due to mononuclear species.

In the amine system the equilibrium constants $K_5(\Delta,\Lambda)$ and $K_5(\Delta,\Delta/\Lambda,\Lambda)$ were calculated as described above for the ammine system, and the results are shown in Tables 4–6. The constant $K_1(\Delta,\Delta/\Lambda,\Lambda)$ was determined as follows. The individual concentrations of the *meso* and *racemic* isomers of the dihydroxo-bridged species could not be determined directly from the IE-HPLC measurements, but their sum was determined. From this value, the known concentration of the cation Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4+}$ and the value of $K_1(\Delta,\Lambda)$ it is possible to calculate the individual concentrations of both dihydroxo-bridged isomers, and thereby also the equilibrium constant $K_1(\Delta,\Delta/\Lambda,\Lambda)$ (Table 2).

Table 5 contains values for the additional equilibrium constants K_3/K_{a3}, K_4 and K_6, which were calculated as described in the Appendix [K_6 is defined in eqns. (5) and (13)].

Table 5. Thermodynamic data for the equilibria between mononuclear and dinuclear species at 25°C in 1 M $NaClO_4$.[a]

Reaction		K/M or 1	$\Delta H°$ /kJ mol^{-1}	$\Delta S°$ /J mol^{-1}K^{-1}
K_3/K_{a3}	(NH$_3$)	2.8(9)×10^7	−47(4)	−17(13)
	(en)	2.5(7)×10^7	−64(9)	−74(28)
	–	[5.0(13)×10^7]		[−68(28)]
K_4	(NH$_3$)	15(5)	−2(4)	13(12)
	(en)	18(5)	−15(8)	−26(27)
	–	[36(10)]		[−20(27)]
K_5	(NH$_3$)	1.1(4)×10^{-2}	−1(4)	−40(11)
	(en)	1.1(3)×10^{-3}	24(4)	23(12)
	–	[2.1(6)×10^{-3}]		[29(12)]
K_6	(NH$_3$)	9(3)×10^{-2}	−12(13)	−64(12)
	(en)	1.2(3)×10^{-2}	13(7)	7(19)
	–	[2.3(6)×10^{-2}]		[13(19)]

[a]The parameters are defined as shown in Scheme 1 and in the Appendix. The parameters for the 1,2-ethanediamine system are for Δ,Λ-isomers and statistically corrected values, given in square brackets, have been calculated as shown previously in the Appendix in Ref. 4.

Kinetics of the cleavage of single bridged species. The cleavage of the monohydroxo-bridged species *cis,cis*-$(H_2O)(NH_3)_4Ir(OH)Ir(NH_3)_4(OH_2)^{5+}$ and Δ,Λ-$(H_2O)(en)_2Ir(OH)Ir(en)_2(H_2O)^{5+}$ (and deprotonated forms), respectively, to their parent mononuclear species were studied spectrophotometrically in the same way as described recently for the analogous rhodium(III) systems.[4,6] The iridium(III) complexes react much slower than their rhodium(III) analogues, but otherwise the present results are very similar to those reported for the rhodium(III) systems.

The cleavage of the monohydroxo-bridged species to give the mononuclear species was studied spectrophotometrically at three temperatures (60.0, 80.0 and 100.3°C) and the hydrogen ion concentration was varied from 10^{-7} to 1.0 M (see Experimental). The visible–ultraviolet spectra of the final solutions were compared with the spectra of solutions of *cis*-$[IrL_4(H_2O)(OH)](ClO_4)_2 \cdot$ nH_2O in 1 M (Na,H)ClO$_4$ with the same [H$^+$]. For acidic solutions, it could be concluded that hydrolysis to mononuclear species is quantitative, as also confirmed by analysis of the product solutions using IE-HPLC. The hydrolysis followed strictly first-order kinetics for the entire reaction.

For solutions with [H$^+$] = 10^{-7} M (1 M NaClO$_4$) a low concentration of iridium(III) ($C_{Ir} = 1.4 \times 10^{-5}$ M) was used in order to eliminate influence from the back-reaction (k_{-5}). However, even with these precautions the hydrolysis in neutral solutions did not follow first-order kinetics, and the spectra never became constant, probably caused by loss of ammonia or 1,2-ethanediamine. This was confirmed by analysis of the product solutions using IE-HPLC, which showed that the hydrolysis primarily gives *cis*-IrL$_4$(H$_2$O)(OH)$^{2+}$ species, but in addition unidentified products were observed and their amount increased with time. First-order constants k_{obs} for 1 M NaClO$_4$ were therefore calculated on the basis of absorbancies measured only during the first part of the reaction (one half half-life) and the spectrum of *cis*-$[Ir(NH_3)_4(H_2O)(OH)](ClO_4)_2 \cdot H_2O$ or *cis*-$[Ir(en)_2$-$(H_2O)(OH)](ClO_4)_2$, respectively, in 1 M NaClO$_4$ were defined as the product spectrum and included the calculations.
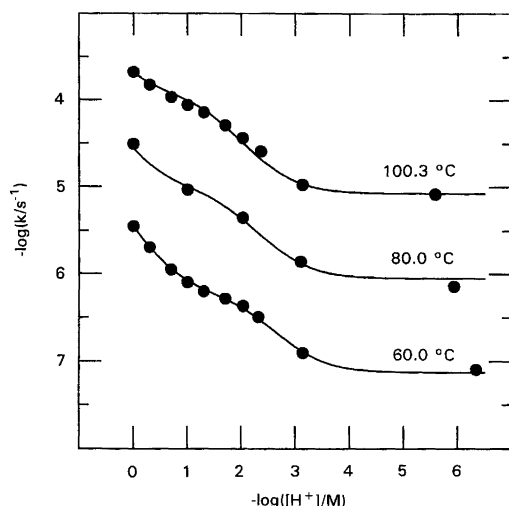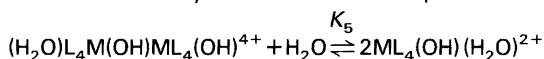
Fig. 3. Observed and calculated (solid line) rate constants for the reaction of the ammine system.

Fig. 4. Observed and calculated (solid line) rate constants for the reaction of the 1,2-ethanediamine system (Δ,Λ).

The observed rate constants vary with [H$^+$] as shown in Figs. 3 and 4. Following the same arguments as discussed for rhodium(III) systems[4,6] the kinetic data for the present systems are interpreted as shown in Scheme 1, which shows the reaction scheme proposed previously for equilibration between monohydroxo- and dihydroxo-bridged species[8,9] supplemented with the possible reactions between the mononuclear species and the mono-hydroxo-bridged species. The equilibration between the dinuclear species is 10^2-10^4 times faster than the cleavage of the monohydroxo-bridged species over the entire [H$^+$] and temperature region, and it therefore follows that the monohydroxo-bridged species are in equilibrium with the dihydroxo-bridged species throughout the entire reaction.

This leads to the rate expression shown in eqn. (1)

$$k_{\text{calc}} = \frac{(k_3/K_{a3})[\text{H}^+]^2 + ak_4[\text{H}^+] + k_5 K_{a1}^{d}}{[\text{H}^+] + K_{a1}^{d}/K_1 + K_{a1}^{d}} \quad (1)$$

in which $a = 1$ for the ammine system and $a = 2$ for the 1,2-ethanediamine system. In the ammine system k_4 corresponds to the cleavage of any of the two Ir–O bonds, while in the amine system it corresponds to the cleavage of one particular bond, as described further in the Appendix.

The parameters for K_1 and K_{a1}^{d} are known (Tables 1 and 2), and the activation parameters for k_3-k_5 were then determined by non-linear least-squares calculations (Table 7 and Figs. 3 and 4). There is a satisfactory agreement between observed and calculated rate constants.

Finally, it is noted that the rate constant k_5 contributes significantly to the values of k_{obs} for 1 M NaClO$_4$ (100%) and for 10^{-3} M HClO$_4$, 1 M NaClO$_4$ (56–78% for the ammine systems and 66–81% for the amine systems). The agreement between the k_{obs} and k_{calc} values for the two media therefore confirms the estimate given for k_5.

The rate constants k_{-3}-k_{-5} for the ammine and the 1,2-ethanediamine systems have been calculated from the

Table 6. Thermodynamic data for the equilibrium at 25°C in 1 M NaClO$_4$.[a]

$$(\text{H}_2\text{O})\text{L}_4\text{M(OH)ML}_4(\text{OH})^{4+} + \text{H}_2\text{O} \xrightleftharpoons{K_5} 2\text{ML}_4(\text{OH})(\text{H}_2\text{O})^{2+}$$

M	L	Configuration	K_5/M	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}	Ref.
Ir(III)	(NH$_3$)$_4$		$1.1(3) \times 10^{-2}$	$-1(4)$	$-40(11)$	This work
Ir(III)	(en)$_2$	Δ,Λ	$1.1(3) \times 10^{-3}$ [$2.1(6) \times 10^{-3}$]	$24(4)$	$23(12)$ [$29(12)$]	This work
Ir(III)	(en)$_2$	Δ,Δ/Λ,Λ	$4.3(9) \times 10^{-3}$	$16(3)$	$10(9)$	This work
Rh(III)	(NH$_3$)$_4$		$1.4(2) \times 10^{-2}$	$12(2)$	$4(4)$	4
Rh(III)	(en)$_2$	Δ,Λ	$7.0(20) \times 10^{-3}$ [$1.4(4) \times 10^{-2}$]	$17(3)$	$14(9)$ [$20(9)$]	4,5
Rh(III)	(en)$_2$	Δ,Δ/Λ,Λ	$2.2(2) \times 10^{-2}$	$17(3)$	$25(4)$	5

[a]The parameters for the ammine system are defined as shown above. The parameters for the 1,2-ethanediamine system are defined as shown in Scheme 2 and in the Appendix. The statistically corrected values, given in square brackets, have been calculated as shown in the Appendix in Ref. 4.
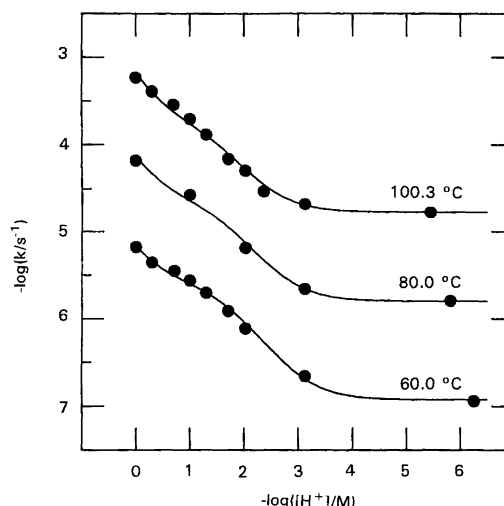
Table 7. Kinetic data for the equilibration between mononuclear and dinuclear species at 25 °C in 1 M NaClO$_4$.[a]

Reaction		k/s^{-1} or $M^{-1}s^{-1}$	$\Delta H^{\neq}/$ kJ mol^{-1}	$\Delta S^{\neq}/$ J mol^{-1} K^{-1}
k_3/K_{a3}	(NH$_3$)	$6.6(18) \times 10^{-8}$	$86.8(54)$	$-91(16)$
	(en)	$2.53(60) \times 10^{-8}$	$118.9(54)$	$8(15)$
k_4	(NH$_3$)	$1.96(25) \times 10^{-9}$	$132.7(20)$	$33(6)$
	(en)	$1.34(21) \times 10^{-8}$	$105.2(26)$	$-43(7)$
	—	$[2.68(42) \times 10^{-8}]$		$[-37(7)]$
k_5	(NH$_3$)	$5.6(11) \times 10^{-10}$	$119.3(30)$	$-22(9)$
	(en)	$6.3(14) \times 10^{-10}$	$124.7(35)$	$-3(10)$
k_{-3}	(NH$_3$)	$2.3(10) \times 10^{-15}$	$134(7)$	$-75(20)$
	(en)	$1.0(4) \times 10^{-15}$	$183(10)$	$82(32)$
	—	$[5.0(20) \times 10^{-16}]$		$[76(32)]$
k_{-4}	(NH$_3$)	$1.3(4) \times 10^{-10}$	$135(5)$	$20(13)$
	(en)	$7.4(23) \times 10^{-10}$	$120(9)$	$-17(28)$
k_{-5}	(NH$_3$)	$5.1(19) \times 10^{-8}$	$119(5)$	$18(14)$
	(en)	$6.0(20) \times 10^{-7}$	$101(6)$	$-26(16)$
	—	$[3.0(10) \times 10^{-7}]$		$[-32(16)]$

[a] The parameters are defined as shown in Scheme 1. Note that for the 1,2-ethanediamine system (Δ,Λ-isomers) the rate constant k_4 is for cleavage of one Ir—O bond as discussed further in the Appendix. Statistically corrected values, given in square brackets, have been calculated as shown previously in the Appendix in Ref. 4.

thermodynamic and kinetic data given above using the formulae given in the Appendix and are listed in Table 7.

Discussion

The reaction scheme for the present iridium(III) systems shown in Scheme 1 is identical to that previously proposed for the corresponding rhodium(III) systems.[4-6] The kinetic and thermodynamic data for the two metal centres are very similar as illustrated by the data shown in Tables 2, 6 and 8. Many of the comments given previously in connection with the rhodium(III) systems are therefore also relevant for the present study and shall only be mentioned briefly here. As expected the iridium(III) complexes react much slower than the rhodium(III) complexes, but the trends on going from ammine to amine species or from meso to racemic amine species are very similar for the two metal centres as discussed below.

For the present iridium(III) complexes a difference between the ammine and meso amine systems is that $\Delta H^{\neq}(k_5)$ and $\Delta S^{\neq}(k_5)$ for the ammine system are smaller than those of the 1,2-ethanediamine system, although the differences are comparable with the standard deviations. A similar, but more pronounced, difference was observed for the analogous rhodium(III) systems and was explained in terms of a different degree of hydrogen-bond stabilization of the aquahydroxo monohydroxo-bridged species.[4] In Scheme 3 it is shown how the aquahydroxo species may exist in two forms, one of which is stabilized by an intramolecular hydrogen bond. The existence of the latter conformation has been established in the solid phase by an X-ray crystal structure determination of the 1,2-ethanediamine iridium(III) complex,[9] and its existence as the dominant form in aqueous solution has been shown unambiguously on the basis of variations in the acid strength of a series of mono- and dinuclear species.[1,8] It follows that the observed rate constant for the cleavage may be expressed as the sum of the rate constants for cleavage of the two species in Scheme 3, which gives eqn. (2), in which the approximation on the right is obtained since $K_H > 10^2$.

$$k_5 = \frac{k_{5b} + k_{5b}K_H}{1 + K_H} \simeq k_{5a}/K_H + k_{5b} \tag{2}$$

As pointed out previously[4] the influence of this stabilization on the kinetics depends on the transition state structure, i.e. if the intramolecular hydrogen bond is broken or not prior to the formation of the transition state. It was shown that the kinetic data for the Rh^{III} system supports the former mechanism, which in terms of Scheme 3 corresponds to $k_{5a}/K_H \gg k_{5b}$. This leads to the approximative expression eqn. (3):

$$k_5 = k_{5a}/K_H \tag{3}$$

and using the known values for K_H the rate constants for cleavage of the non-hydrogen-bond stabilized species may then be calculated. The results are shown in Table 8 together with the published data for the rhodium(III) system. Since the rate constant k_4 also refers to cleavage of species, which are not hydrogen-bond stabilized, it seems reasonable to expect the two ratios $k_{5a}(en)/k_{5a}(NH_3)$ and $k_4(en)/k_4(NH_3)$ to be similar. This is seen to be the case (Table 8), and it is further noted that nearly the same

Table 8. Calculation of the rate constant $k_{5a} = k_5/K_H$ for cleavage of the non-hydrogen-bonded species (H$_2$O)L$_4$M(OH)ML$_4$-(OH)$^{4+}$ shown in Scheme 3.

M	L$_4$	Configuration	k_5/s^{-1} [a]	K_H [b]	k_{5a}/s^{-1} [a]	$k_{5a}(en)/k_{5a}(NH_3)$	$k_4(en)/k_4(NH_3)$ [c]
Rh(III)	(NH$_3$)$_4$		1.56×10^{-7}	$10^{2.4}$	3.9×10^{-5}	7.4	10.1
Rh(III)	(en)$_2$	Δ,Λ	2.30×10^{-7}	$10^{3.1}$	2.9×10^{-4}		
Ir(III)	(NH$_3$)$_4$		5.6×10^{-10}	$10^{2.6}$	2.2×10^{-7}	5.9	13.7
Ir(III)	(en)$_2$	Δ,Λ	6.3×10^{-10}	$10^{3.3}$	1.3×10^{-6}		

[a] The parameters for Rh(III) are from Ref. 4. [b] From Refs. 1 and 8. [c] k_4 is the statistically corrected constant in the case of the 1,2-ethanediamine complexes.
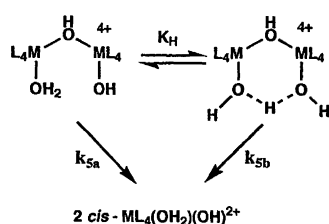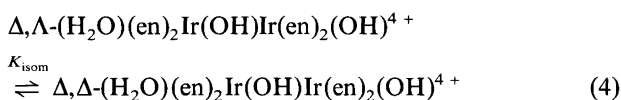
2 cis - ML$_4$(OH$_2$)(OH)$^{2+}$

Scheme 3. The monohydroxo-bridged aquahydroxo species may exist in two conformations, and it is proposed that the intramolecular hydrogen-bonded form is significantly more stable kinetically than is the other conformation.

ratio was found for the rhodium(III) system. This result supports our earlier proposal that the transition-state structure does not (to any large extent) involve a hydrogen bond between M–OH and M–OH$_2$.

The variation of the equilibrium constants K_4–K_6 for the present iridium(III) species is nearly the same for the ammine and amine systems with the order $K_4 \gg K_5 < K_6$ for both systems (Table 5). The same trend was reported for the rhodium(III) systems and the significant stabilization of the 4 + charged monohydroxo-bridged species was explained in terms of the intramolecular hydrogen-bond stabilization of this species (the expected order, on basis of charge considerations alone, is $K_4 > K_5 > K_6$).[4]

The $\Delta H°$ and $\Delta S°$ values for K_5 in the ammine and amine systems are similar for rhodium(III) and iridium(III), and the variations in K_5 are less than a factor of 10 (Table 6). From the values of K_5 the relative stability of the *meso* and *racemic* isomers of the monohydroxo-bridged amine species may be expressed by K_{isom} as shown in eqn. (4):

$$\Delta,\Lambda\text{-}(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4\ +}$$

$$\overset{K_{isom}}{\rightleftharpoons} \Delta,\Delta\text{-}(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)^{4\ +} \qquad (4)$$

and can be determined from the relation $K_{isom} = K_5(\Delta,\Lambda)/K_5(\Delta,\Delta/\Lambda,\Lambda)$. For iridium(III) the value $K_{isom} = 0.25$ is calculated from the data given in Table 6, and this value is very close to $K_{isom} = 0.33$ previously reported for the rhodium(III) complexes.[5] Both values are close to the statistically expected ratio of 0.5, indicating that intramolecular interactions, which could alter this ratio, for each metal ion are likely to be similar for the two diastereoisomers and also similar for the two metal ions.

With the present data for the *racemic* iridium(III) amine system it is now possible to compare the ratio $K_1(\Delta,\Lambda/K_1(\Delta,\Delta)$ for the three metal centres Cr^{III}, Rh^{III} and Ir^{III}. From the data in Table 2 we calculate the ratios 3.4, 5.9 and 5.8, respectively. It is striking how close the ratios for rhodium(III) and iridium(III) are, but even the ratio for chromium(III) is close to that for the two other metal ions. This illustrates the general observation[1] that the hydroxo-bridged complexes of these three metal ions have many properties in common and often show the same trends for variations in the ligand sphere.

Conclusions

It is concluded that the present new data for the iridium(III) ammine and 1,2-ethanediamine systems show trends which are parallel to those obtained for the rhodium(III) systems, and thereby support the mechanistic and thermodynamic results presented earlier. The new data have made it possible to study further the variation imposed by changing the non-bridging ligands, and this has added new evidence in favour of earlier proposals. The reactions between the mono- and dinuclear species can be understood fairly well in terms of the properties known from the substitution chemistry of the mononuclear species and properties which are due to the interactions between the two metal centers. Of the latter type intramolecular hydrogen-bond formations are of particular importance, as also found for the reactions between monohydroxo- and dihydroxo-bridged species. Strong evidence points to the proposals that this type of interaction, not only thermodynamically, but also kinetically tends to stabilize the dinuclear species. The hydroxo-bridged complexes of iridium(III) have many properties in common with those of chromium(III) and in particular of rhodium(III), and the hydroxo-bridged complexes of the three metal ions often show the same trends for variations in the ligand sphere.

Appendix

In the ammine system the equilibrium constants K_3–K_5 and their respective rate constants are defined as shown in Scheme 1. K_6 is defined in eqn. (5):

$$K_6 =$$

$$\frac{[cis\text{-}Ir(NH_3)_4(H_2O)(OH)^{2\ +}][cis\text{-}Ir(NH_3)_4(OH)_2^+]}{[cis,cis\text{-}(HO)(NH_3)_4Ir(OH)Ir(NH_3)_4(OH)^{3\ +}]}$$

$$(5)$$

The constants K_3, K_4 and K_6 were calculated using eqns. (6)–(9):

$$K_3/K_{a3} = k_3K_{a3}/k_{-3} = K_{a1}{}^dK_5/(K_{a1}{}^m)^2 \qquad (6)$$

$$K_4 = k_4/k_{-4} = K_{a1}{}^dK_5/K_{a1}{}^m \qquad (7)$$

$$K_5 = k_5/k_{-5} \qquad (8)$$

$$K_6 = K_{a2}{}^mK_5/K_{a2}{}^d \qquad (9)$$

The rate constants for the condensation reactions were then calculated from the known constants for the cleavage reactions using eqns. (6)–(8).

In the 1,2-ethanediamine system the equilibrium constants K_3-K_6 and their respective rate constants are defined as shown below [dimer^{4+} = (HO)(en)$_2$Ir-(OH)Ir(en)$_2$(OH$_2$)$^{4+}$ etc. and monomer^{2+} = cis-Ir(en)$_2$-(OH)(OH$_2$)$^{2+}$ etc.]:

$$K_3/K_{a3} = (k_3/K_{a3})/k_{-3}$$

$$= \frac{[\Delta\text{-monomer}^{3+}][\Lambda\text{-monomer}^{3+}]}{[\Delta,\Lambda\text{-dimer}^{5+}][H^+]} \quad (10)$$

$$K_4 = k_4/k_{-4}$$

$$= \frac{[\Delta\text{-monomer}^{3+}][\Lambda\text{-monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{5+}]}$$

$$= \frac{[\Delta\text{-monomer}^{2+}][\Lambda\text{-monomer}^{3+}]}{[\Delta,\Lambda\text{-dimer}^{5+}]} \quad (11)$$

$$K_5 = k_5/k_{-5} = \frac{[\Delta\text{-monomer}^{2+}][\Lambda\text{-monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{4+}]} \quad (12)$$

$$K_6 = \frac{[\Delta\text{-monomer}^{2+}][\Lambda\text{-monomer}^{+}]}{[\Delta,\Lambda\text{-dimer}^{3+}]}$$

$$= \frac{[\Delta\text{-monomer}^{+}][\Lambda\text{-monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{3+}]} \quad (13)$$

It is noted that k_4 is the microscopic rate constant for the cleavage of one particular Ir–O bond, while k_3 and k_5 correspond to the cleavage of one of the two Ir–O bonds. Likewise, k_{-4} is the microscopic rate constant for the formation of the dinuclear species from one of the two different enantiomeric pairs of mononuclear species. The constants $k_{-3}-k_{-5}$ were then calculated using eqns. (10)–(13).

The equilibrium constants $K_i(\Delta,\Delta/\Lambda,\Lambda) = K_i(\Delta,\Delta) = K_i(\Lambda,\Lambda)$ are defined as exemplified in eqn. (14):

$$K_4 = k_4/k_{-4}$$

$$= \frac{[\Delta\text{-monomer}^{3+}][\Delta\text{-monomer}^{2+}]}{[\Delta,\Delta\text{-dimer}^{5+}]}$$

$$= \frac{[\Lambda\text{-monomer}^{3+}][\Lambda\text{-monomer}^{2+}]}{[\Lambda,\Lambda\text{-dimer}^{5+}]} \quad (14)$$

References

1. Springborg, J. In: A. G. Sykes, Ed. *Advances in Inorganic Chemistry*, Academic Press, San Diego 1988, Vol. 32, p. 55.
2. Baes, C. F. and Mesmer, R. E. *Hydrolysis of Cations*, Wiley, New York 1976.
3. Andersen, P. *Coord. Chem. Rev. 94* (1989) 47.
4. Springborg, J. *Acta Chem. Scand. 46* (1992) 956.
5. Bjerrum, M. J., Kaas, K., Larsen, E., Nielsen, B. and Springborg, J. *Inorg. Chem. 28* (1989) 532.
6. Kaas, K. and Springborg, J. *Inorg. Chem. 26* (1985) 387.
7. Galsbøl, F. and Rasmussen, B. *Acta Chem. Scand., Ser. A 38* (1984) 141.
8. Galsbøl, F., Simonsen, K. and Springborg, J. *Acta Chem. Scand. 46* (1992) 915.
9. Galsbøl, F., Larsen, S., Rasmussen, B. and Springborg, J. *Inorg. Chem. 25* (1986) 290.
10. Christensson, F. and Springborg, J. *Acta Chem. Scand., Ser. A 36* (1982) 21.
11. Christensson, F. and Springborg, J. *Acta Chem. Scand. 24* (1985) 2129.
12. Springborg, J. and Toftlund, H. *Acta Chem. Scand., Ser. A 30* (1976) 171.
13. Christensson, F., Springborg, J. and Toftlund, H. *Acta Chem. Scand., Ser. A 34* (1980) 317.
14. Hancock, M., Nielsen, B. and Springborg, J. *Acta Chem. Scand., Ser. A 36* (1982) 313.