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Procedures are given for the preparation of salts of the following complex cations: cis-[Ir(NH₃)₆(OH)(H₂O)]³⁺, trans-[Ir(NH₃)₆(OH)(H₂O)]²⁺, [(NH₃)₆Ir(OH)]Ir(NH₃)₆⁻ and cis,cis-[{H₂O(NH₃)}Ir(OH)(NH₃)₆]²⁻. The concentration acid dissociation constants of cis- and trans-[Ir(NH₃)₆(H₂O)]³⁺ and cis,cis-[{H₂O(NH₃)}Ir(OH)(NH₃)₆]²⁻ were determined in 1.0 M NaClO₄. The thermodynamics and kinetics for the equilibration reaction between the dihydroxoo-bridged and the monohydroxoo-bridged species were studied spectrophotometrically from 25.0 to 80.0 °C for concentrations of H⁺ ranging from 10⁻⁷ to 1.0 M (1.0 M (Na,H)ClO₄), and the results have been interpreted in terms of Scheme 1 of the paper.

Hydrolysis of aquated metal ions to form hydroxo-bridged polynuclear complexes has been reported for most transition metals and is of great significance in the aqueous chemistry of such ions. An important reaction in the initial stage of these polymerization reactions is the equilibrium between the monohydroxoo- and dihydroxoo-bridged species, exemplified in Scheme 1 for the ammine iridium(III) system.

Equilibria of this kind have been studied extensively during the last two decades. The mechanistic aspects of this type of reaction are now fairly well understood and have been thoroughly discussed in recent reviews.¹,² Bridge formation and bridge cleavage occur by an uncatalyzed pathway, which for all systems is the dominant path in weakly acidic solutions, and by an acid-catalyzed pathway, which often is the dominant path in strongly acidic solutions. The acid-catalyzed path is believed to involve the intermediate formation of a labile aqua-bridged species. The formation of an intramolecular hydrogen bond in the monohydroxoo-bridged species between terminally coordinated water and hydroxide plays an important feature. In Scheme 2 it is shown how the aquahydroxy 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 a crystal structure determination of the 1,2-ethanediamine iridium(III) analogue.³ Its existence as the dominant form in aqueous solution has been shown unambiguously on the basis of variations in the acid dissociation constants of a series of mono- and binuclear species, and estimates of the equilibrium constant Kₑ have been given (see also later). Kinetic and thermodynamic properties of the complexes have been correlated with the strength of the intramolecular hydrogen bond as discussed in Ref. 1.

The ammine and 1,2-ethanediamine (meso as well as racemic isomers) species of chromium(III) and rhodium (III) have all been studied.¹,²,⁴-⁹ Recently a study of the

Scheme 1. Reaction scheme for the equilibration between monohydroxoo- and dihydroxoo-bridged species.

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iridium(III) 1,2-ethanediamine species (meso) was reported, and in this paper we have studied the last member in this series, the ammine iridium(III) species.

Preparatively this work is a continuation of previous studies of the syntheses of mononuclear iridium(III) ammine and amine complexes and the binuclear amine complexes. The syntheses of pentaamminechloro-, tetraamminechloro- and triamminechloroiridium(III) complexes were reported recently, and the cis- and trans-dichlorotetraamineiridium(III) species serve as starting materials for the complexes synthesized in this work.

Experimental

Materials. The preparation of cis- and trans-[Ir(NH₃)₄Cl₂]Cl has been described previously. All other reagents were of analytical grade.

Instrumentation. The purity of the products was checked by chromatography on a Pharmacia FPLC instrument equipped with a Mono Q cation exchange column. Absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer after the solutions had been filtered through Millipore filters No. HAWPO 1300, 0.45 μm. A Perkin-Elmer Lambda diode array 3840 spectrophotometer was used for spectral measurements in the kinetic investigations. Thermogravimetric measurements were performed on the thermobalance described by Pedersen. The [H⁺] measurements were carried out using a Radiometer PHM52 digital pH-meter equipped with a G202C glass electrode and a K401 calomel electrode, also from Radiometer. In the latter electrode the initial saturated potassium chloride solution was replaced with 1.0 M sodium chloride solution. X-Ray powder diffraction photographs were taken with a Hagg–Guinier focusing camera XDC 700 calibrated with silicon and using CuKα radiation.

Analyses. C, H, N, Cl, Br and S analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

Synthetic procedures

1. cis-[aquahydroxotetraamineiridium(III)] perchlorate monohydrate. A 2.00 g sample of cis-[Ir(NH₃)₄Cl₂]Cl·½H₂O (5.32 mmol) [or an equivalent amount of the perchlorate salt (2.24 g)] and 1.6 g of NaOH (40 mmol) were dissolved in 75 ml of water and the solution was refluxed for 3 h. After cooling to room temperature the solution was evaporated on a rotating vacuum evaporator (bath temperature 40°C) to a volume of ca. 25 ml, and the diaqua complex was precipitated by dropwise addition of 25 ml of 70% HClO₄ with stirring and cooling in ice. The mixture was left at −15°C for 2 h to complete the crystallization before the precipitate was filtered off and dried as much as was possible using suction. The crude cis-[Ir(NH₃)₄(H₂O)₂](ClO₄)₂·aq was extracted on the filter with small portions of hot water (a total of 8 ml). As the pH of the filtrate was adjusted to 7.2 by addition of 5 M NaOH (ca. 3 ml) a copious precipitate was formed. 10 ml of a saturated NaClO₄ solution (ca. 150 g of NaClO₄ · H₂O in 50 ml of water) were then added to the suspension, and the mixture was left at room temperature for 2 h before it was cooled at 5°C overnight. The crystals were filtered off and washed, first with two 3 ml portions of 50% ethanol, then 96% ethanol, finally with diethyl ether, and dried in air. Yield: 2.5 g (92%) of cis-[Ir(NH₃)₄(OH)(H₂O)](ClO₄)₂ · H₂O. (Found: H 3.18; N 10.79; Cl 13.95. Calc. for IrH₁₄N₄ClO₇: H 3.35; N 10.94; Cl 13.84).

2. cis-[aquahydroxotetraamineiridium(III)] dithionite. To 2.40 g of cis-[Ir(NH₃)₄(OH)(H₂O)](ClO₄)₂ · H₂O (4.69 mmol) were added 20 ml of a saturated Na₂S₂O₄ solution (ca. 20 g of Na₂S₂O₄ · 2H₂O in 100 ml of water), and the suspension was stirred for 1 h at room temperature before the precipitate was filtered off, washed with 96% ethanol and diethyl ether and dried in air. The product (2.1 g) was then dissolved in 35 ml of water by boiling. The mixture was filtered and 25 ml of a saturated Na₂S₂O₄ solution were added to the filtrate. The mixture was left for crystallization, first at room temperature then at 5°C overnight. The crystals were filtered off and washed, first with two 5 ml portions of 50% ethanol, then with 96% ethanol, finally with diethyl ether, and dried in air. Yield: 1.8 g (86%) of cis-[Ir(NH₃)₄(OH)(H₂O)](ClO₄)₂ · S₂O₄ · H₂O. (Found: H 3.27; N 12.26; S 13.90. Calc. for IrH₁₄N₄S₂O₈: H 3.32; N 12.30; S 14.08). Thermogravimetry: loss of weight 39.4 mg per g sample, i.e. 18.0 g mol⁻¹ (see Results).

3. trans-[aquahydroxotetraamineiridium(III)] perchlorate. A 2.00 g sample of trans-[Ir(NH₃)₄Cl₂]Cl·H₂O (5.20 mmol) [or an equivalent amount of the perchlorate salt (2.24 g)] and 1.2 g of NaOH (30 mmol) were mixed with 60 ml of water in a Teflon container. The container was closed and heated to 100°C for 96 h. (After 1 h the mixture was stirred...
Table 1. Thermodynamic parameters for cis- and trans-tetraamminediaqua
diaquiridium(III) complexes at 25°C.¹

<table>
<thead>
<tr>
<th>Complex</th>
<th>Constant</th>
<th>Value</th>
<th>( \Delta H^\circ \text{kJ mol}^{-1} )</th>
<th>( \Delta S^\circ \text{J mol}^{-1} \text{K}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>( pK_{a1} )</td>
<td>6.265(7)</td>
<td>44.8(12)</td>
<td>30(4)</td>
</tr>
<tr>
<td></td>
<td>( pK_{a2} )</td>
<td>8.088(9)</td>
<td>46.6(12)</td>
<td>1(4)</td>
</tr>
<tr>
<td>trans</td>
<td>( pK_{a1} )</td>
<td>5.214(8)</td>
<td>44.6(12)</td>
<td>50(4)</td>
</tr>
<tr>
<td></td>
<td>( pK_{a2} )</td>
<td>8.052(9)</td>
<td>46.1(13)</td>
<td>0(5)</td>
</tr>
</tbody>
</table>

¹In this and the following tables the standard deviations are given in parentheses; i.e. 44.8 (12) means 44.8 ± 1.2.

to ensure complete dissolution.) The dark-brown solution was filtered and the filtrate evaporated on a rotating vacuum
evaporator (bath temperature 40°C) to a volume of ca. 10 ml, and the diaqua complex was precipitated by drop-
wise addition of 10 ml of 70% HClO₄ with stirring and cooling in ice. The mixture was left at −15°C overnight
before the precipitate was filtered off and dried as much as was possible using suction. The crude trans-[Ir(NH₃)₅-
(H₂O)][(ClO₄)]₂ was extracted on the filter with small portions of hot water (a total of 5 ml). The small (ca. 0.04
g) yellow residue was trans-[Ir(NH₃)₅Cl][ClO₄]. When the pH of the filtrate was adjusted to 6.6 by addition of 5 M NaOH
(ca. 3 ml) a copious precipitate was formed. 10 ml of a saturated NaClO₄ solution were then added to the suspen-
sion and the mixture was cooled at 5°C overnight. The brownish precipitate was filtered off, washed, first with
96% ethanol and then with diethyl ether, and dried in air. Yield: 2.2 g (84%) of crude product. This product was
dissolved in 25 ml of water by heating, and 0.15 g of SP Sephadex C-25 was added. The suspension was stirred for 1
min before it was filtered and the residue was washed with 2 ml of water. 0.10 g of acetic acid was added to the
combined filtrate and washings. After the acetic acid had dissolved, 15 ml of a saturated NaClO₄ solution were added
and the solution cooled in ice. The almost-white precipitate was isolated as described above. Yield: 1.8 g (70%) of trans-
[Ir(NH₃)₅(OH)(H₂O)][ClO₄]₂. (Found: H 2.98; N 11.28; Cl 14.20. Calc. for IrH₃N₅ClO₄·H₂O: H 3.06; N 11.34; Cl 14.35).

4. Di-μ-hydroxobis[tetraammineiridium(III)] bromide tetrahydrate. Solid cis-[Ir(NH₃)₅(OH)(H₂O)]S₂O₈, 1.80 g
(3.95 mmol), was heated to 180°C for 2.5 h (the loss of weight was 0.071 g corresponding to 2.0 mol of H₂O per
mol of dimer). To the resulting crude [(NH₃)₅Ir(OH)]₂-
Ir(NH₃)₅][S₂O₈] was added 20 ml of a saturated NH₄Br
solution (ca. 100 g of NH₄Br in 100 ml of water) and the suspension was stirred for 1.5 h at room temperature.
The crude bromide salt was filtered off and washed with two 5
ml portions of ice-cold 50% ethanol. The product was then
dissolved by extraction on the filter with small portions of
water at room temperature (a total of 35 ml). 25 ml of a
saturated NH₄Br solution were added to the filtrate and the
mixture cooled in ice for 2 h before the pale-yellow crystals
were filtered off and washed, first with two 5 ml portions of
ice-cold 50% ethanol, then with 96% ethanol, finally with
diethyl ether, and dried in air. Yield: 1.5 g (80%) of
[(NH₃)₅Ir(OH)]Ir(NH₃)₅][Br]·4H₂O. (Found: H 3.51; N 11.82; Br 33.88. Calc. for IrH₃N₅Br·4O·H₂O: H 3.62; N 11.84; Br 33.78).

5. Di-μ-hydroxobis[tetraammineiridium(III)] perchlorate dihydrate. A mixture of 7 ml of a saturated NaClO₄ solu-
tion and 5 ml of water was added to the corresponding bromide, 1.40 g (1.48 mmol). The suspension was stirred
for 1 h with cooling in ice. The crude perchlorate was filtered off and dried as much as was possible using suction
before it was dissolved by extraction on the filter with three
5 ml portions of water at room temperature. 10 ml of a satura-
ted NaClO₄ solution were then added to the filtrate and
the mixture was cooled in ice for 30 min. The pale-
yellow crystals were filtered off, washed with 96% ethanol and
diethyl ether, and dried in air. Yield: 1.4 g (96%) of
[(NH₃)₅Ir(OH)]Ir(NH₃)₅][ClO₄]·2H₂O. (Found: H 2.95; N 11.21; Cl 14.84. Calc. for IrH₃N₅ClO₄·2H₂O: H 3.06; N 11.34; Cl 14.35). Addition of sodium dithionate to an aqueous solution of the perchlorate salt yields pure
[(NH₃)₅Ir(OH)]Ir(NH₃)₅][S₂O₈].

6. cis,cis-aquatetraammineiridium(III)-μ-hydroxyhydroxy-
tetraammineiridium(III)] perchlorate monohydrate. To 1.00 g
of [(NH₃)₅Ir(OH)]Ir(NH₃)₅][ClO₄]·2H₂O (1.01 mmol) were added 2.00 ml of 1.00 M HClO₄. The suspension was
stirred at 40 ± 1°C and a clear yellow solution was formed
within 20 min. After further 40 min of heating 2.00 ml of
1.00 M NaOH were added followed by 2 ml of a saturated
NaClO₄ solution. The mixture was cooled in ice for 30 min
before the crystals were filtered off, washed with 96% ethanol and diethyl ether, and dried in air. The crude
product (0.9 g) was extracted on the filter with small portions
of water at room temperature (a total of 5 ml). To the
filtrate was added 5 ml of a saturated NaClO₄ solution.
The mixture was left at room temperature for 15 min and then
cooled in ice for 30 min. The crystals were filtered off,
washed with 96% ethanol and diethyl ether and dried in air.
Yield: 0.83 g (83%) of cis,cis-[{H₂O(NH₃)₅Ir(OH)-
Ir(NH₃)₅}[O(H₂O)][ClO₄]·H₂O. (Found: H 2.88; N 11.17; Cl 14.56. Calc. for IrH₃N₅ClO₄·H₂O: H 3.06; N 11.34; Cl 14.35).

Table 2. Thermodynamic parameters for the binuclear ammine
and amine species at 25°C.⁸

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>( \Delta H^\circ \text{kJ mol}^{-1} )</th>
<th>( \Delta S^\circ \text{J mol}^{-1} \text{K}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1 )</td>
<td>(NH₃)</td>
<td>3.3(6)</td>
<td>−2.4(33)</td>
</tr>
<tr>
<td></td>
<td>(en)</td>
<td>5.7(8)</td>
<td>−1.5(47)</td>
</tr>
<tr>
<td>( pK_{a1} )</td>
<td>(NH₃)</td>
<td>3.115(4)</td>
<td>42.5(7)</td>
</tr>
<tr>
<td></td>
<td>(en)</td>
<td>1.91(2)</td>
<td>10.8(67)</td>
</tr>
<tr>
<td>( pK_{a2} )</td>
<td>(NH₃)</td>
<td>9.012(8)</td>
<td>58.9(12)</td>
</tr>
<tr>
<td></td>
<td>(en)</td>
<td>9.04(3)</td>
<td>53.3(50)</td>
</tr>
</tbody>
</table>

⁸The constants are defined as shown in Scheme 1. The values for the 1,2-ethanediamine species (en) are from Ref. 3 and are for the Δ,Δ isomers.
Table 3. Spectrophotometrically determined equilibrium constants, $K_i$, in 1 M NaClO₄.

<table>
<thead>
<tr>
<th>$\Delta\bar{\nu}/^\circ$ C</th>
<th>$K_i$(obs)</th>
<th>$K_i$(calc)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>3.3</td>
<td>2.7</td>
</tr>
<tr>
<td>80.0</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>60.0</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>40.0</td>
<td>3.0</td>
<td>3.2</td>
</tr>
<tr>
<td>34.6</td>
<td>3.7</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*Calculated from the values of $\Delta H^\circ$ and $\Delta S^\circ$ given in Table 2.

Thermogravimetry: loss of weight 19.9 mg per g sample, i.e. 19.7 g mol$^{-1}$.

Determination of acid dissociation constants. The concentration acid dissociation constants of cis- and trans-[Ir(NH$_3$)$_6$(H$_2$O)$_2$]$_2$$^{4+}$ and cis,cis-[H$_2$(H$_2$O)(NH$_3$)$_5$Ir(OH)Ir(NH$_3$)$_5$(H$_2$O)$_2$]$^{14+}$ were determined as described by Mønsted and Mønsted$^{15}$ by regression analysis of the titration data from dissolution of the perchlorates in an excess of HClO$_4$ and titration with NaOH. The determinations were made at 25 and 40$^\circ$C in 1.0 M NaClO$_4$. The results for cis- and trans-[Ir(NH$_3$)$_6$(H$_2$O)$_2$]$_2$$^{4+}$ are given in Table 1 and the results for cis,cis-[H$_2$(H$_2$O)(NH$_3$)$_5$Ir(OH)Ir(NH$_3$)$_5$(H$_2$O)$_2$]$^{14+}$ are given in Table 2.

Determination of the equilibrium constant, $K_i$. Equilibrium solutions were obtained by heating solutions of [(NH$_3$)$_2$Ir(OH)Ir(NH$_3$)$_5$](ClO$_4$)$_4$·2H$_2$O in 1 M NaClO$_4$, kept in glass ampoules at 34.6, 40.0, 60.0, 80, and 100$^\circ$C for 34 days, 12 days, 29 h, 2 h, and 18 min, respectively. The spectra of these solutions did not change upon further heating, showing that equilibrium had been attained. The equilibrium constants were then calculated from these spectra together with the spectra of the pure species, [(NH$_3$)$_2$Ir(OH)Ir(NH$_3$)$_5$]$_2$$^{14+}$ and cis,cis-[H$_2$(H$_2$O)(NH$_3$)$_5$Ir(OH)Ir(NH$_3$)$_5$(H$_2$O)]$^{14+}$. These calculations were in each experiment based upon absorbances measured at 51 different wavelengths in the region 250–300 nm. A single experiment, performed at 100$^\circ$C, in which the solution initially contained the pure cis,cis-[H$_2$(H$_2$O)(NH$_3$)$_5$Ir(OH)Ir(NH$_3$)$_5$(H$_2$O)]$^{14+}$, gave a value of $K_i$ identical to the value when starting with the dihydroxy-bridged species. The thermodynamic parameters for $K_i$ are given in Tables 2 and 3.

Kinetic measurements. The reactant solutions in 1 M (Na,H)ClO$_4$ were from 1.0 to 2.0 mM in [(NH$_3$)$_2$Ir(OH)Ir(NH$_3$)$_5$](ClO$_4$)$_4$·2H$_2$O. The reactions had half-lives from 5 min to 2 days under the conditions used. Therefore, the fast reactions were monitored by repetitive scanning and the slow reactions were measured using aliquots of the solution kept separately in glass ampoules in the dark. The hydrogen ion concentration changed slightly during a kinetic experiment. The hydrogen ion concentration in the original solutions of the binuclear species and in the equilibrium solutions, [H$^+$]$_0$ and [H$^+$]$_{eq}$, respectively, were calculated from the solution stoichiometry using the thermodynamic parameters given in Table 2 and [H$^+$]$_{eq}$ = $\sqrt{[H^+_0] + [H^+]_{eq}}$. For solutions with [H$^+$]$_{eq} > 0.05$ M the change in the hydrogen ion concentration was less than 1%. At lower [H$^+$] larger variations were calculated (7% for [H$^+$]$_{eq} = 0.005$ M), but in this region the observed dependence of $k_{obs}$ on [H$^+$] was small. For reactions in pure 1 M NaClO$_4$ it was checked by glass-electrode measurements that the pH in the final equilibrium solution was 6.1 ± 0.1 (at 25$^\circ$C), close to the value calculated from the p$K_a$-values given in Table 2. The influence of [H$^+$] on $k_{obs}$ is negligible at low [H$^+$], and it was therefore concluded that pseudo first-order conditions could be assumed. Pseudo first-order rate constants, $k_{obs}$, were calculated as described previously. In each kinetic run the rate constants were calculated from absorbances measured at 161 different wavelengths in the region 240–400 nm. All kinetic experiments were performed in duplicate, and the reproducibility was within 4%. The activation parameters were fitted by minimizing the sum of (ln $k_{obs}$ - ln $k_{calc}$)$^2$, the value of $k_{calc}$ being defined by eqn. (1) in combination with the expression $k = (k_B T/h) exp (\Delta S^R/RT - \Delta H^R/RT)$.

Results

Syntheses and structural assignments. cis- and trans-[Ir(NH$_3$)$_6$(H$_2$O)(OH)]$^{4+}$ have been prepared by base hydrolysis of their parent dichloro species as the corresponding 1,2-ethanediamine iridium(III) complexes$^{13}$ with some

![Absorption spectra of cis- and trans-][Ir(NH$_3$)$_6$(H$_2$O)]$^{4+}$ in 0.1 M HClO$_4$.](attachment:image.png)
minor modifications: It was necessary first to isolate the very soluble [Ir(NH₃)₃(H₂O)][(ClO₄)₂]·aq salt in order to obtain pure compounds. Additionally, treatment with SP Sephadex C-25 and ascorbic acid was necessary to remove higher charged by-products and to suppress oxidation of pure trans-[Ir(NH₃)₃(H₂O)(OH)][(ClO₄)₂].

trans-[Ir(NH₃)₃Cl₂]⁺ reacts stereoregenterently when it undergoes base hydrolysis, in contrast to trans-[Ir(en)₂Cl₂]⁺. The assignments of the cis- and trans-[Ir(NH₃)₃(H₂O)-(OH)]⁺ species were based upon their electronic absorption spectra in acidic solution (Fig. 1) as compared with the spectra of the corresponding 1,2-ethanediamine species. Additional evidence for the assignments of the geometrical isomers is that cis-[Ir(NH₃)₃(H₂O)(OH)]SO₄, like the analogous compounds of Cr(III), Rh(III) and Ir(III) with either ammonia or 1,2-ethanediol as ligands, liberates approximately 1 mol of H₂O per mol of metal (Fig. 2) forming the binuclear dihydroxo-bridged species. The trans-complexes do not undergo dimerization. Finally, the pK₅-values of the diaqua-species were used for the prepared according to standard procedures. Heating of solid cis-[Ir(NH₃)₃(H₂O)](OH)₃SO₄ yields [(NH₃)Ir(OH)₂Ir(NH₃)₃][(ClO₄)₂] almost quantitatively. This salt was used to isolate pure [(NH₃)Ir(OH)Ir(NH₃)₃]Br₄·4H₂O, from which pure [(NH₃)Ir(OH)Ir(NH₃)₃][(ClO₄)₂]·2H₂O could be prepared. Hydrolysis of the latter complex in acidic solution followed by addition of base and NaClO₄ led to cis,cis-[(HO)(NH₃)₂Ir(OH)Ir(NH₃)₃(H₂O)][(ClO₄)₂]·H₂O. The proposed dihydroxo- and monohydroxo-bridged structures of [(NH₃)Ir(OH)Ir(NH₃)₃][(ClO₄)₂]·2H₂O and of cis,cis-[(HO)(NH₃)₂Ir(OH)Ir(NH₃)₃(H₂O)][(ClO₄)₂]·H₂O, respectively, are unambiguous and are based upon the spectral properties, the acid-base reactions and the equilibria reactions which are discussed in the following. Additionally, the X-ray diffraction powder diagram of pure [(NH₃)Ir(OH)Ir(NH₃)₃][(ClO₄)₂] showed a pattern similar to that of the corresponding rhodium(III) compound, for which the configuration is well established. Acid-base properties. The concentration acid dissociation constants of the coordinated water ligands in cis- and trans-[Ir(NH₃)₃(H₂O)]⁺ are of the same order of magnitude as for the corresponding 1,2-ethanediame iridium(III) complexes. Table 4 gives a comparison with some relevant literature data. The pK₅-values of the trans-isomers tend to be lower than the pK₅*-values of the corresponding cis-isomers, and ΔpK₅ ≈ pK₅* is larger for the trans-isomers than for the cis-isomers. This is as observed for the analogous 1,2-ethanediame complexes. The pK₅*-values of cis,cis-[(HO)(NH₃)₂Ir(OH)Ir(NH₃)₃(H₂O)]⁺ (Table 2) are discussed later (see Discussion). The spectrum of cis,cis-[(HO)(NH₃)₂Ir(OH)Ir(NH₃)₃(H₂O)]⁺ was obtained by measuring basic solutions of cis,cis-[(HO)(NH₃)Ir(OH)Ir(NH₃)₃(H₂O)][(ClO₄)₂]·H₂O. Identical spectra were obtained in 0.1 M NaOH, 0.9 M NaClO₄ and in 0.005 M NaOH, 1.0 M NaClO₄. This shows that deprotonation of the hydroxo bridge does not occur in this region, and therefore pK₅*(μ-OH) > 14. The spectra of [(NH₃)Ir(OH)Ir(NH₃)₃][(ClO₄)₂]·2H₂O were identical for [H⁺] varying from 10⁻⁷ to 1.0 M. This is in agreement with the dihydroxo-bridged structure, showing that protonation of the hydroxo bridge does not occur even in the most acidic solutions, and it is concluded that pK₅a < −1 (Scheme 1). In the same way it was shown that deprotonation of one of the hydroxo bridges in the dihydroxo-bridged complex does not occur in 0.1 M NaOH, 0.9 M

Table 4. pK₅* Values for some cis- and trans-tetraamminediaqua complexes.*

<table>
<thead>
<tr>
<th></th>
<th>cis</th>
<th>trans</th>
<th>Medium</th>
<th>T/°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pK₅*</td>
<td>pK₅a</td>
<td>ΔpK₅</td>
<td>pK₅*</td>
<td>pK₅a</td>
</tr>
<tr>
<td>[Cr(NH₃)₃(H₂O)]²⁺</td>
<td>4.96</td>
<td>7.53</td>
<td>2.57</td>
<td>4.38</td>
<td>7.78</td>
</tr>
<tr>
<td>[Co(NH₃)₃(H₂O)]²⁺</td>
<td>5.89</td>
<td>7.99</td>
<td>2.10</td>
<td>4.92</td>
<td>8.26</td>
</tr>
<tr>
<td>[Rh(NH₃)₃(H₂O)]²⁺</td>
<td>6.40</td>
<td>8.32</td>
<td>1.92</td>
<td>5.21</td>
<td>8.05</td>
</tr>
<tr>
<td>[Ir(NH₃)₃(H₂O)]²⁺</td>
<td>6.26</td>
<td>8.09</td>
<td>1.83</td>
<td>5.21</td>
<td>8.05</td>
</tr>
</tbody>
</table>

*ΔpK₅ = pK₅a − pK₅*.
NaClO₃, and the hydroxo bridge must therefore have pKₐ (μ-OH)₂ > 14.

Equilibration of the binuclear species. The binuclear species cis,cis-[H₂O(NH₃)₃]Ir(OH)Ir(NH₃)₃[H₂O]⁺⁺ (and its deprotonated form) and [(NH₃)₃Ir(OH)]Ir(NH₃)₃[OH]⁺⁺ equilibrate in neutral and acidic solutions. In acidic solution these equilibria (with equilibrium constants K₁ and K₉ in Scheme 1) are shifted almost completely to the monohydroxo-bridged diaqua species. A spectroscopic determination of the equilibrium constant K₁ is therefore not possible in this region. Equilibrium studies were therefore restricted to neutral solutions. An analysis of the UV spectra confirmed the presence of only two species, cis,cis-[(HO)(NH₃)₂]Ir(OH)Ir(NH₃)₃[H₂O]⁺⁺ and [(NH₃)₃]Ir(OH)₂Ir(NH₃)₃][OH]⁺⁺, as illustrated in Fig. 3. The equilibrium constant, K₁, was calculated from the spectral measurements and led to the results shown in Tables 2 and 3 (see also Experimental).

The kinetics of the equilibration reaction was studied spectrophotometrically at four temperatures, 25.0, 39.8, 58.9 and 80.0°C. The hydrogen ion concentration was varied from 10⁻² to 1 M. The change in absorbance with time (Fig. 4) followed first-order kinetics throughout the entire reaction. The observed rate constants vary with [H⁺] as shown in Fig. 5. The observed [H⁺] dependence is consistent with Scheme 1, in agreement with the reaction scheme proposed previously for equilibration between monohydroxo- and dihydroxo-bridged species of Cr(III), Rh(III) and Ir(III). This scheme leads to eqn. (1).

\[
K_{rate} = k_1 + \frac{k_{-2}K[H^+]}{K_{st}} + \frac{k_{i}K_{st}/K_1 + k_{-2}[H^+]^2}{[H^+]^2 + K_{st}}
\]  

It should be noted that when K₉ > 10 M, as shown above, the aqua-bridged species will never attain a stoichiometrically significant concentration. It follows that only the ratio k₂/K₉, and not k₂ and K₉, can be determined. k₁ and k⁻² were determined by non-linear least-squares calculations using eqn. (1) with values for K₁ and K₉ obtained from the experiments described above. The values for k⁻¹ and k₂/K₉ were calculated using the relations K₁/K₉ = (k₂/K₉)k⁻² and K₁ = k₁/k⁻₁. It is seen that there is a satisfactory agreement between the observed and the calculated rate constants (Fig. 5) and that all the parameters are well defined (Table 5).

Discussion

The reaction scheme for the equilibration between the monohydroxo- and dihydroxo-bridged species for the present ammine system is shown in Scheme 1 and is identical to that proposed for the 1,2-ethanediamine system. The kinetic and thermodynamic data for the two systems are similar and show the same trends (Tables 2 and 5). Most of the comments given previously in connection with the 1,2-ethanediamine system are therefore also relevant for the present study and shall only be mentioned briefly here.

The two pKₐ-values for the monohydroxo-bridged species are separated by 5.90 units. This is much larger than
that observed for the corresponding mononuclear species \( \Delta P K_a = 1.8 \), but is less than the value found for the corresponding monohydroxyl-bridged complex with 1,2-ethanediamine \( \Delta P K_a = 7.1 \) (Table 2). As discussed above, large \( \Delta P K_a \)-values have been explained in terms of intramolecular hydrogen-bond stabilization of the aqua- hydroxy species of the binuclear complexes (Scheme 2). Estimates of the equilibrium constant \( K_{HH} \) (Scheme 2) have been made as described previously and are given in Table 6. The value for the present system confirms the trends already noted: the stabilization increases in the order Cr(III) < Rh(III) < Ir(III), and for all three metal ions it is found that the ratio \( K_{HH}(en)/K_{HH}(NH_3) \) is constant, from 5 to 6 at 25°C.

The hydrogen-bond stabilization of the aqua-hydroxy monohydroxyl-bridged species has a strong influence on the kinetics of the bridge formation reaction, \( k_{-1} \). In Scheme 2 it is proposed how the aqua-hydroxy monohydroxyl-bridged species may form the dihydroxyl-bridged species by two different routes, leading (when \( K_{HH} \gg 1 \)) to the expression for \( k_{-1} \) shown in eqn. (2). According to this scheme the

\[
k_{-1} = k_{-1a}/K_{HH} + k_{-1b}
\]

formation of the dihydroxyl-bridged species may be characterized by the following two extreme situations: \( k_{-1a}/k_{-1b} \gg K_{HH} \) and \( k_{-1a}/k_{-1b} \ll K_{HH} \). The first situation corresponds to bridge formation via the \( k_{-1a} \) path and the second to bridge formation via the \( k_{-1b} \) path. At present it is not possible to exclude either of these possibilities.

Our previous discussions have essentially been based upon the assumption that the hydrogen-bonded conformation is the reactive species, i.e. eqn. (2) is simplified to \( k_{-1} = k_{-1b} \). It was assumed that the formation of the transition state would require a weakening (or cleavage) of the intramolecular hydrogen bond, and that the hydrogen-bonded conformation would resemble the transition state more than other conformations. An increase in the strength of the hydrogen bond might therefore contribute to the activation parameters by an increase of the activation enthalpy and the activation entropy. This trend was found for the ammine and amine systems of Cr(III) and Rh(III). Furthermore, for both metal ions it was found that the increase of \( \Delta S^\ddagger \) was greater than the increase in \( \Delta H^\ddagger \), i.e. the strength of the hydrogen bond increases as the rate of equilibration increases.

Apparently, the kinetic data for the corresponding iridium(III) system do not follow this trend. The activation parameters for \( k_{-1} \) are nearly identical for the ammine and the amine systems. One explanation might be that the conclusions from the model above are invalidated, as the M-O bonds are affected by the non-bridging nitrogen ligands. Another factor is that the substitution reactions in the chromium(III) systems are probably essentially associative, while a large degree of dissociative character for rhodium(III), and particularly for iridium(III), is expected. Since an increase in the dissociative character might facilitate a reaction path via the non-hydrogen-bonded conformation \( (k_{-1a}) \), it seems reasonable to consider this alternative limiting case. The assumption that the cleavage occurs via the non-hydrogen-bonded species, \( k_{-1a} \), leads to the approximative expression shown in eqn. (3).

\[
k_{-1} = k_{-1a}/K_{HH}
\]
Table 7. The ratio, $k_{14}/k_{2}$, for the two bridge-formation reactions at 25°C.

<table>
<thead>
<tr>
<th>L₄</th>
<th>Cr(III)</th>
<th>Rh(III)</th>
<th>Ir(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)L₄</td>
<td>22,300</td>
<td>370</td>
<td>320</td>
</tr>
<tr>
<td>(en)₃L₂</td>
<td>≥46,500⁹</td>
<td>990</td>
<td>1100</td>
</tr>
</tbody>
</table>

*See Schemes 1 and 2. *Only a lower limit for the chromium(III) amine system can be estimated, since in this case only an upper limit to $k_{2}$ has been reported.¹

s⁻¹ and $k_{14}$(en) = $5.2 \times 10^{-4}$ s⁻¹. The rate constants for the corresponding chromium(III) and rhodium(III) systems may be calculated from the data given in Refs. 4 and 6-8: for the rhodium(III) systems the constants are $k_{14}$(NH₄) = $3.5 \times 10^{-3}$ s⁻¹ and $k_{14}$(en) = $5.1 \times 10^{-2}$ s⁻¹, and for chromium(III) the constants are $k_{14}$(NH₃) = $6.0 \times 10^{-2}$ s⁻¹ and $k_{14}$(en) = 9.3 s⁻¹.

The ratio of the rate constants for the two bridge-formation reactions, $k_{14}/k_{2}$, can now be calculated and are given in Table 7. The data clearly reflect that coordinated hydroxide is a much better nucleophile than coordinated water, since all ratios are very large. The ratios are nearly identical for rhodium(III) and chromium(III), while the ratios for the two chromium(III) complexes are 50 times (or more) larger than those for the other two metal ions. This demonstrates the well established fact that rhodium(III) and iridium(III) are more dissociative in their substitution reactions than chromium(III). For all three metal ions the ratios increase in the order NH₃ < en, suggesting that this associate character increases in that order.

The present kinetic data do not make it possible to determine the dominant reaction path in Scheme 2. The discussion above in terms of the two limiting cases must be considered with the reservations already mentioned. Furthermore, an interchange between the two extremes might occur along the series Cr(III), Rh(III) and Ir(III). This could mean that the chromium(III) species reacts predominantly via the hydrogen-bonded conjugation while the iridium(III) species react predominantly via the non-hydrogen-bonded isomer.

The bridge cleavage may occur by an acid-catalyzed or an uncatalyzed path. The former is proposed to involve the intermediate formation of an aqua-bridged species. From the spectral data it is concluded that the aqua bridge is a strong acid, with $\text{p}\text{K}_a < -1$. It has been suggested⁴ that the $\text{p}\text{K}_a$-values of such aqua bridges are about $-5$, but experimental evidence has not been reported. The ratio $[\text{H}^+]k_{14}/K_{\text{aq}}/k_{2}$ gives the ratio between the rates of acid-catalyzed and uncatalyzed bridge cleavage. At $[\text{H}^+] = 1 \text{ M}$ it is 1600 for the present iridium(III) ammine system, while it is 160 for the amine system. The corresponding values for the rhodium(III) systems are 1700 and 300, but the ratio is only 0.4 for the ammine chromium(III) system.⁵ This has been explained by different acid strengths of the aqua bridges,⁶ but different reactivities of the aqua-bridged species (relative to the hydroxy-bridged species) can not be excluded.

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References

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