The Preparation and Characterization of cis- and trans-Aqua hydroxobis(1,2-ethanedi amine)iridium(III) Complexes

FRODE GALSBOŁ and BIRGITTE S. RASMUSSEN

Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

A yield of 80 % of cis-[Ir(en)$_2$(OH)(H$_2$O)]S$_2$O$_6$ (en=1,2-ethanedi amine) is obtained by base hydrolysis of cis-[Ir(en)$_2$Cl$_2$Cl] (ca. 0.4 M NaOH, reflux for 2 h) followed by adjustment of pH to 7.0 and precipitation with Na$_2$S$_2$O$_6$. By base hydrolysis of trans-[Ir(en)$_2$Cl$_2$Cl] (ca. 0.5 M NaOH, 100 °C for 96 h) followed by adjustment of pH to 6.5 and precipitation with NaClO$_4$ a crude, approx. 3:2 mixture of cis- and the hitherto unknown trans-[Ir(en)$_2$(OH)(H$_2$O)] (ClO$_4$)$_2$ is obtained in ca. 80 % yield. The geometrical isomers are separated by recrystallization. In addition to chemical analysis the compounds have been characterized by their electronic spectra and by potentiometric titrations. The concentration acidity constants of cis- and trans-[Ir(en)$_2$(H$_2$O)$_2$] are estimated to be $K_{s1}=10^{-6.200±0.007}$, $K_{s2}=10^{-8.979±0.009}$ mol/l and $K_{s3}=10^{-4.798±0.004}$, $K_{s4}=10^{-7.856±0.010}$ mol/l (25 °C, 1 M NaCl), respectively.

The preparation of cis-[Ir(en)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$ (en=1,2-ethanedi amine) via the base hydrolysis of cis-[Ir(en)$_2$Cl$_2$]Cl reported by Baranovskii et al. is tedious from the preparative point of view as it involves ion-exchange chromatography to remove chloride ions from the solution, and furthermore the yield is not specified. The product is described as a strongly hygroscopic white-cream-coloured mass. Ford et al. prepared cis-[Ir(en)$_2$(OH)$_3$]Cl$^+$ photochemically from both cis- and trans-[Ir(en)$_2$Cl$_2$]Cl$^+$ in basic solution but the product was not isolated. As the related ions cis-[M(en)$_2$(OH)(H$_2$O)]$^{2+}$ (M=Cr(III)$^+$, Co(III)$^+$, and Rh(III)$^+$) are easily precipitated from aqueous solution as dionate salts, we found it conceivable that the corresponding iridium compound could be isolated in the same way. In the present paper we describe a synthetic procedure, based upon that of Baranovskii et al., which gives a ca. 80 % yield of cis-[Ir(en)$_2$(OH)(H$_2$O)]S$_2$O$_6$ by base hydrolysis of cis-[Ir(en)$_2$Cl$_2$]Cl$^+$ followed by adjustment of pH to favour the aquahydroxo species and precipitation with sodium dithionate solution.

Baranovskii et al. have observed that trans-[Ir(en)$_2$Cl$_2$]$^+$ does not undergo inner-sphere substitution when boiled for 30 h with a large excess of KBr, KI, KNO$_2$, or KSCN. Bauer and Basolo showed that under more severe conditions (reflux for 45 h or heating at 140 °C for 2 h) inner-sphere substitution does take place. Bauer and Basolo also report that both cis- and trans-[Ir(en)$_2$Cl$_2$]Cl$^+$ undergo base hydrolysis with retention of geometry (2h at 140 °C in a Na$_2$HPO$_4$-NaOH buffer at pH 11.5), but they have not isolated the products. We find that by prolonged treatment of trans-[Ir(en)$_2$Cl$_2$]Cl with ca. 0.5 M NaOH (100 °C for 96 h) followed by adjustment of pH to 6.5 and precipitation with sodium perchlorate a crude, approx. 3:2 mixture of cis- and the hitherto unknown trans-[Ir(en)$_2$(OH)(H$_2$O)] (ClO$_4$)$_2$ is obtained in ca. 80 % yield. The geometrical isomers are easily separated by recrystallization as the perchlorate of the trans-isomer is much less soluble than that of the cis-isomer. On the contrary, the dionate of the cis-isomer is much less soluble than that of the trans-isomer.

In addition to chemical analysis cis- and trans-[Ir(en)$_2$(OH)(H$_2$O)]$^{2+}$ have been identified by potentiometric titrations and characterized by the electronic spectra of their conjugate acids and bases.
EXPERIMENTAL

Materials. cis- and trans-[Ir(en)₂Cl₂]Cl were prepared as described earlier. The cis-isomer was recrystallized from water (ca. 3 ml/g of complex). The trans-isomer was used without further purification.

Instrumentation. Absorption spectra were recorded on a Cary 118C spectrophotometer after the solutions had been filtered on Gelman Acrodisc filters No. 4192, 0.2 μm. Thermogravimetric measurements were performed on the thermobalance described by Pedersen. The pH measurements were carried out using a Radiometer PHM52 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.

SYNTHETIC PROCEDURES

1. cis-[aquahydroxobis(1,2-ethanediamine)tridium(III)] dihionate. A 3.0 g sample of cis-[Ir(en)₂Cl₂]Cl·H₂O (6.9 mmol) and 1.6 g of NaOH (40 mmol) are dissolved in 90 ml of water and the solution is refluxed for 2 h. After cooling to room temperature, pH is adjusted to ca. 7 by addition of 12 M HCl (ca. 2.8 ml). The solution is filtered and the filtrate is evaporated on a rotating vacuum evaporator, RVE, (bath temperature 40 °C) to a volume of ca. 20 ml. pH is adjusted to 7.0 and 20 ml of a saturated NaN₂S₂O₅ solution (ca. 20 g of NaN₂S₂O₅·2H₂O in 100 ml of water) are added over a period of ca. 10 min. (within a few min. white crystals start to precipitate) and the mixture is cooled in iced-water for 1 h. The precipitate is filtered, washed, first with three 2 ml portions of ice-cold water, then

Fig. 1. The absorption spectra of cis-[Ir(en)₂(OH)(H₂O)] (ClO₄)₂ dissolved (A) in 0.1 M HClO₄ (C=6.4×10⁻³ mol/l), (B) in H₂O (C=2.3×10⁻³ mol/l), and (C) in 0.01 M NaOH (C=3.2×10⁻⁴ mol/l), respectively. Consult text for discussion of the spectrum in NaOH.

two times with ethanol, finally with ether, and dried in air. Yield 2.8 g (80 %) of cis-
[Ir(en)$_2$(OH)(H$_2$O)]S$_2$O$_6$. (Found: C 9.40; H 3.84; N 10.88; S 12.76. Calc. for IrC$_2$H$_9$N$_4$S$_2$O$_8$:
C 9.47; H 3.77; N 11.04; S 12.64.) Thermogravimetry: loss of weight 40.9 mg/g sample, i.e. 20.9
mg/mol (see discussion section).

2. cis- and trans-[aquahydroxobis(1,2-
ethanediamine)iridium(III)] perchlorate. A 3.0 g
sample of trans-[Ir(en)$_2$Cl$_2$]Cl (7.2 mmol) and 1.8
g of NaOH (45 mmol) are dissolved in 90 ml of
water in a teflon container. The container is
closed, placed in an oven, and heated to 100 °C
for 96 h. The yellow solution is acidified with 5 ml
of 70 % HClO$_4$ (ca. 60 mmol) and evaporated on
an RVE (bath temperature 40 °C) to a volume of
ca. 20 ml. The small yellow precipitate (trans-
[Ir(en)$_2$Cl$_2$]ClO$_4$, ca. 0.1 g) is filtered and washed
with 1–2 ml of water and pH of the filtrate and
washings is adjusted to 6.5 with 2 M NaOH (ca. 9
ml) which results in a copious precipitate. Then
30 ml of a saturated NaClO$_4$-solution (ca. 150 g
NaClO$_4$.H$_2$O in 50 ml of water) are added to the
suspension, and the mixture is cooled in the
refrigerator overnight. The slightly cream-coloured precipitate is filtered, washed, first with
two 3 ml portions of 1:1 ethanol–water, then with
ethanol, finally with ether, and dried in air. Yield
3.2 g (82 %) of a mixture of cis- and trans-
[Ir(en)$_2$(OH)(H$_2$O)](ClO$_4$)$_2$. Comparison of the
electronic spectrum of the product mixture dis-
solved in 0.1 M acid with the spectra of cis- and
trans-[Ir(en)$_2$(H$_2$O)$_2$]Cl$_2$ (Figs. 1 and 2) indicates
the mixture to contain ca. 60 % of the cis- and ca.
40 % of the trans-isomer. The mixture is dis-
solved in 20 ml of water by boiling and the
solution is allowed to stand for crystallization of the
trans-isomer, first 2 h at room temperature.

Fig. 2. The absorption spectra of trans-[Ir(en)$_2$(OH)(H$_2$O)](ClO$_4$)$_2$ dissolved (A) in 0.1 M HClO$_4$
($C=1.0 \times 10^{-2}$ mol/l), (B) in H$_2$O ($C=2.5 \times 10^{-2}$ mol/l), and (C) in 0.01 M NaOH ($C=4.5 \times 10^{-4}$ mol/l),
respectively. Consult text for discussion of the spectrum in NaOH.

then in the refrigerator overnight. The crystals are isolated by filtration and washed, first with two 2 ml portions of 1:1 ethanol–water, then with ethanol, finally with ether, and dried in air. Yield 1.5 g of crude trans-[Ir(en)₂(OH)(H₂O)](ClO₄)₂.

To the mother liquor are added 20 ml of a saturated NaClO₄-solution (alternatively the slightly soluble dithionate salt can be precipitated, see preparation 1) and the solution is allowed to stand overnight for crystallization. The crystals are filtered and washed, first with two 2 ml portions of 1:1 ethanol–water, then with ethanol, finally with ether, and dried in air. Yield 1.4 g (35 %) of cis-[Ir(en)₂(OH)(H₂O)](ClO₄)₂. (Found: C 8.71; H 3.64; N 10.30; Cl 12.79. Calc. for IrC₁₂H₁₉N₄Cl₂O₁₀: C 8.79; H 3.51; N 10.26; Cl 12.98).

The crude trans-isomer is extracted with 5 ml (pipette) of 1.0 M HClO₄. The solution is filtered and the flask and filter are washed with 5 ml of water. 5 ml (pipette) of 1.0 M NaOH are added to the filtrate and washings. The precipitate formed is dissolved by boiling and the solution is allowed to stand overnight for crystallization. (Big crystals are produced if the solution is not agitated when the crystallization sets in). The crystals are filtered and washed, first with two 2 ml portions of 1:1 ethanol/water, then with ethanol, finally with ether, and dried in air. Yield 1.4 g (35 %) of trans-[Ir(en)₂(OH)(H₂O)](ClO₄)₂. (Found: C 8.73; H 3.66; N 10.30; Cl 12.78. Calc. for IrC₁₂H₁₉N₄Cl₂O₁₀: C 8.79; H 3.51; N 10.26; Cl 12.98).

RESULTS AND DISCUSSION

We have demonstrated that trans-[Ir(en)₂Cl₂]⁺ does not necessarily react stereoreententively when it undergoes base hydrolysis. The reaction of trans-[Ir(en)₂Cl₂]Cl with 1,2-ethanediamine (1:10 dissolved in a little water and heated at 170 °C for 10 h) also results in a rearrangement as the main product is [Ir(en)₃]Cl₃.

The absorption spectra of cis-[Ir(en)₂(OH)(H₂O)](ClO₄)₂ dissolved in 0.1 M HClO₄, H₂O, and 0.01 M NaOH, respectively, are shown in Fig. 1. They are in reasonable agreement with earlier published results. Fig. 2 shows the absorption spectra of the corresponding trans-species. The absorption bands at 212–213 nm of the solutions in NaOH (the molar absorptivities can be reproduced within ca. ±3 %) probably do not belong (entirely) to transitions in the complexes but are caused by an excess of OH⁻ in the reference cell equal to the concentration of [Ir(en)₂(OH)]⁺ in the sample cell (OH⁻ has ε=ca. 10³ mol⁻¹ cm⁻¹ at 200 nm).

The concentration acidity constants for cis- and trans-[Ir(en)₂(H₂O)]³⁺ were estimated by regression analysis as described by Mønsted and Mønsted11 of the titration data from dissolution of the hydroxo species in excess HClO₄ and back titration with NaOH. The results are (25 °C, Kₐ’s in mol/l): cis-[Ir(en)₂(OH)(H₂O)]SO₄: Kₐ₁=10⁻⁶.1.45±0.008, Kₐ₂=10⁻⁸.001±0.011 (1.0 M NaClO₄), cis-[Ir(en)₂(OH)(H₂O)](ClO₄)₂: Kₐ₁=10⁻⁶.290±0.007, Kₐ₂=10⁻⁸.097±0.009 (1.0 M NaCl), trans-[Ir(en)₂(OH)(H₂O)](ClO₄)₂: Kₐ₁=10⁻⁴.796±0.004, Kₐ₂=10⁻⁷.856±0.010 (1.0 M NaCl). The trans-isomer could not be titrated in 1.0 M NaClO₄ as trans-[Ir(en)₂(OH)(H₂O)](ClO₄)₂ precipitates during the titration (the solution was ca. 10⁻³ M with respect to the complex ion). Table 1 shows a comparison with relevant literature data. By dissolution in an excess of 0.1 M NaOH and back titration with 0.1 M HCl on a Radiometer ETS822 titration system, the titration curves shown in Fig. 3 are obtained. The pKₐ-values for the cis-isomer determined from the titration curve correspond very well with the

<table>
<thead>
<tr>
<th>Metal</th>
<th>cis</th>
<th>trans</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pKₐ₁</td>
<td>pKₐ₂</td>
<td>Δₐcis</td>
<td>pKₐ₁</td>
</tr>
<tr>
<td>Cr</td>
<td>4.75</td>
<td>7.35</td>
<td>2.60</td>
<td>4.12</td>
</tr>
<tr>
<td>Co</td>
<td>6.06</td>
<td>8.19</td>
<td>2.13</td>
<td>4.45</td>
</tr>
<tr>
<td>Rh</td>
<td>6.34</td>
<td>8.24</td>
<td>1.90</td>
<td>4.47</td>
</tr>
<tr>
<td>Ir</td>
<td>6.29</td>
<td>8.10</td>
<td>1.81</td>
<td>4.80</td>
</tr>
</tbody>
</table>

Table 1. pKₐ values (25 °C) for some complexes of the type [M(en)₂(H₂O)₂]³⁺. Δ=pKₐ₂−pKₐ₁ of en=1,2-ethanediamine.
cis- and trans-[Ir(en)$_2$(OH)(H$_2$O)](ClO$_4$)$_2$, respectively, in an excess of 0.1 M NaOH and back titration with 0.1 M HCl.

values published by Baranovskii et al.\textsuperscript{1} (5.6 and 7.8). The spectra and the acidity constants show that the assignments of the geometrical isomers are correct. Additional evidence for this is that, like the analogous Rh complex,\textsuperscript{14} cis-[Ir(en)$_2$(OH)(H$_2$O)]$S_2$O$_6$ on heating liberates approx. 1 mol of H$_2$O per mol of metal (Fig. 4) and forms the dimer\textsuperscript{15} $\Delta$,$\Lambda$-[en$_2$Ir(OH)$_2$Ir(en)$_2$]$S_2$O$_6$. The elemental analyses – see experimental section – show that the starting material does not contain water of crystallization. cis-[Ir(en)$_2$(OH)(H$_2$O)](ClO$_4$)$_2$ does not form a dimer on heating but starts to decompose at ca. 140 °C.

Acknowledgements. The authors wish to thank Dr. Ole Mønsteds for lending us his regression analysis computer program. We also thank Johnson, Matthey & Co. for a loan of the iridium chloride used in these studies.

REFERENCES


Received June 29, 1983.