Acta Chemica Scandinavica A 38 (1984) 141–146

The Preparation and Characterization of *cis*- and *trans*-Aquahydroxobis(1,2-ethanediamine)iridium(III) Complexes

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A yield of 80 % of *cis*-$[Ir(en)_2(OH)(H_2O)]S_2O_6$ (en=1,2-ethanediamine) is obtained by base hydrolysis of *cis*-$[Ir(en)_2Cl_2]Cl$ (*ca.* 0.4 M NaOH, reflux for 2 h) followed by adjustment of pH to 7.0 and precipitation with $Na_2S_2O_6$. By base hydrolysis of *trans*-$[Ir(en)_2Cl_2]Cl$ (*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*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ 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*-$[Ir(en)_2(H_2O)_2]^{3+}$ are estimated to be $K_{a1}=10^{-6.290\pm0.007}$, $K_{a2}=10^{-8.097\pm0.009}$ mol/l and $K_{a1}=10^{-4.798\pm0.004}$, $K_{a2}=10^{-7.856\pm0.010}$ mol/l (25 °C, 1 M NaCl), respectively.

The preparation of *cis*-$[Ir(en)_2(H_2O)_2](ClO_4)_3$ (en=1,2-ethanediamine) *via* the base hydrolysis of *cis*-$[Ir(en)_2Cl_2]Cl$ reported by Baranovskii *et al.*[1] 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.*[2] prepared *cis*-$[Ir(en)_2(OH)_2]^+$ photochemically from both *cis*- and *trans*-$[Ir(en)_2Cl_2]^+$ in basic solution but the product was not isolated. As the related ions *cis*-$[M(en)_2(OH)(H_2O)]^{2+}$ (M=Cr(III)[3], Co(III)[4], and Rh(III)[5] are easily precipitated from aqueous solution as dithionate 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.*[1], which gives a *ca.* 80 % yield of *cis*-$[Ir(en)_2(OH)(H_2O)]S_2O_6$ by base hydrolysis of *cis*-$[Ir(en)_2Cl_2]^+$ followed by adjustment of pH to favour the aquahydroxo species and precipitation with sodium dithionate solution.

Baranovskii *et al.*[6] have observed that *trans*-$[Ir(en)_2Cl_2]^+$ 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[7] showed that under more severe conditions (reflux for 65 h or heating at 140 °C for 2 h) inner-sphere substitution does take place. Bauer and Basolo[7,8] also report that both *cis*- and *trans*-$[Ir(en)_2Cl_2]^+$ undergo base hydrolysis with retention of geometry (2h at 140 °C in a Na_2HPO_4-NaOH buffer at pH 11.5), but they have not isolated the products. We find that by prolonged treatment of *trans*-$[Ir(en)_2Cl_2]Cl$ 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*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ 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 dithionate of the *cis*-isomer is much less soluble than that of the *trans*-isomer.

In addition to chemical analysis *cis*- and *trans*-$[Ir(en)_2(OH)(H_2O)]^{2+}$ have been identified by potentiometric titrations and characterized by the electronic spectra of their conjugate acids and bases.

0302-4377/84 $2.50

EXPERIMENTAL

Materials. *cis-* and *trans*-$[Ir(en)_2Cl_2]Cl$ were prepared as described earlier.[9] 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.[10] 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) iridium(III)*] *dithionate.* A 3.0 g sample of *cis*-$[Ir(en)_2Cl_2]Cl.H_2O$ (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 $Na_2S_2O_6$-solution (*ca.* 20 g of $Na_2S_2O_6.2H_2O$ 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 icewater for 1 h. The precipitate is filtered, washed, first with three 2 ml portions of ice-cold water, then

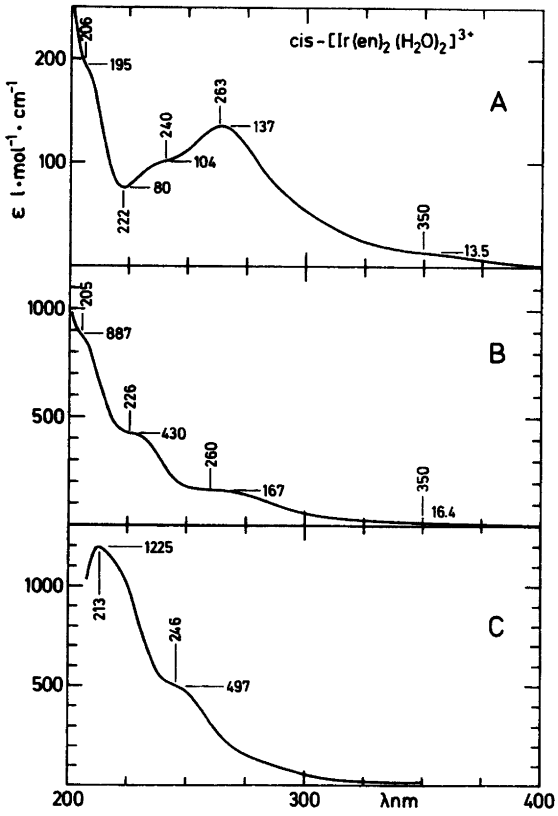

Fig. 1. The absorption spectra of *cis*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ dissolved (A) in 0.1 M $HClO_4$ ($C \simeq 6.4\times10^{-3}$ mol/l), (B) in H_2O ($C \simeq 2.3\times10^{-3}$ mol/l), and (C) in 0.01 M NaOH ($C \simeq 3.2\times10^{-4}$ mol/l), respectively. Consult text for discussion of the spectrum in NaOH.

two times with ethanol, finally with ether, and dried in air. Yield 2.8 g (80 %) of *cis*-$[Ir(en)_2(OH)(H_2O)]S_2O_6$. (Found: C 9.40; H 3.84; N 10.88; S 12.76. Calc. for $IrC_4H_{19}N_4S_2O_8$: 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 g/mol (see discussion section).

2. cis- *and* trans-[*aquahydroxobis(1,2-ethanediamine)iridium(III)*] *perchlorate.* A 3.0 g sample of *trans*-$[Ir(en)_2Cl_2]Cl$ (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*-$[Ir(en)_2Cl_2]ClO_4$, *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 $NaClO_4.H_2O$ 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*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$. Comparison of the electronic spectrum of the product mixture dissolved in 0.1 M acid with the spectra of *cis*- and *trans*-$[Ir(en)_2(H_2O)_2]^{3+}$ (Figs. 1 and 2) indicates the mixture to contain *ca.* 60 % of the *cis*- and *ca.* 40 % of the *trans*-isomer. The mixture is dissolved 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

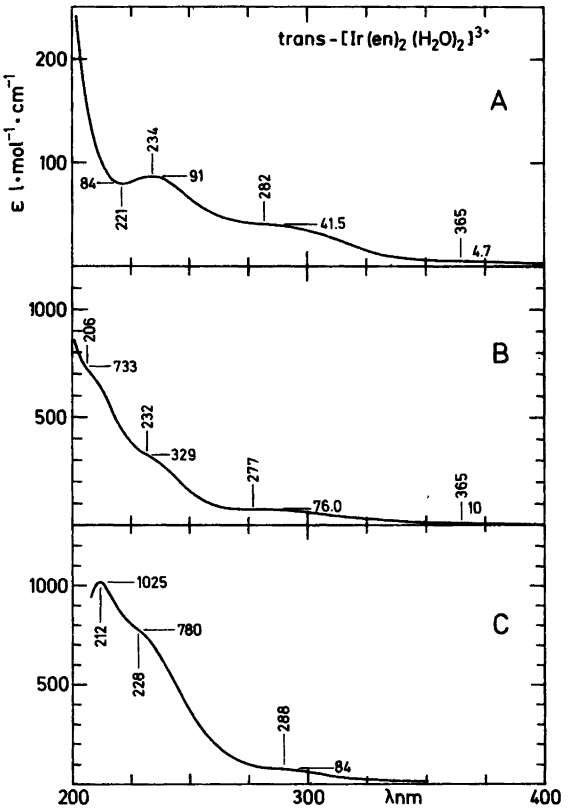

Fig. 2. The absorption spectra of *trans*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ dissolved (A) in 0.1 M $HClO_4$ ($C \simeq 1.0\times10^{-2}$ mol/l), (B) in H_2O ($C \simeq 2.5\times10^{-3}$ mol/l), and (C) in 0.01 M NaOH ($C \simeq 4.5\times10^{-4}$ mol/l), respectively. Consult text for discussion of the 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*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$.

To the mother liquor are added 20 ml of a saturated $NaClO_4$-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*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$. (Found: C 8.71; H 3.64; N 10.30; Cl 12.79. Calc. for $IrC_4H_{19}N_4Cl_2O_{10}$: 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 $HClO_4$. 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*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$. (Found: C 8.73; H 3.66; N 10.30; Cl 12.78. Calc. for $IrC_4H_{19}N_4Cl_2O_{10}$: C 8.79; H 3.51; N 10.26; Cl 12.98).

RESULTS AND DISCUSSION

We have demonstrated that *trans*-$[Ir(en)_2Cl_2]^+$ does not necessarily react stereorententively when it undergoes base hydrolysis. The reaction of *trans*-$[Ir(en)_2Cl_2]Cl$ 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 $[Ir(en)_3]Cl_3$.

The absorption spectra of *cis*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ dissolved in 0.1 M $HClO_4$, H_2O, and 0.01 M NaOH, respectively, are shown in Fig. 1. They are in reasonable agreement with earlier published results.[1,2] 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 $[Ir(en)_2(OH)_2]^+$ in the sample cell (OH^- has $\varepsilon = ca.\ 10^3$ l mol^{-1} cm^{-1} at 200 nm).

The concentration acidity constants for *cis*- and *trans*-$[Ir(en)_2(H_2O)_2]^{3+}$ were estimated by regression analysis as described by Mønsted and Mønsted[11] of the titration data from dissolution of the hydroxoaqua species in excess $HClO_4$ and back titration with NaOH. The results are (25 °C, K_a's in mol/l): *cis*-$[Ir(en)_2(OH)(H_2O)]S_2O_6$: $K_{a1}=10^{-6.145\pm0.008}$, $K_{a2}=10^{-8.001\pm0.011}$ (1.0 M $NaClO_4$), *cis*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$: $K_{a1}=10^{-6.290\pm0.007}$, $K_{a2}=10^{-8.097\pm0.009}$ (1.0 M NaCl), *trans*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$: $K_{a1}=10^{-4.798\pm0.004}$, $K_{a2}=10^{-7.856\pm0.010}$ (1.0 M NaCl). The *trans*-isomer could not be titrated in 1.0 M $NaClO_4$ as *trans*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ 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 pK_a-values for the *cis*-isomer determined from the titration curve correspond very well with the

Table 1. pK_a values (25 °C) for some complexes of the type $[M(en)_2(H_2O)_2]^{3+}$. $\Delta = pK_{a2} - pK_{a1}$. en=1,2-ethanediamine.

Metal	*cis*			*trans*			Medium	Ref.
	pK_{a1}	pK_{a2}	Δ_{cis}	pK_{a1}	pK_{a2}	Δ_{trans}		
Cr	4.75	7.35	2.60	4.12	7.71	3.59	1.0 M $NaClO_4$	11
Co	6.06	8.19	2.13	4.45	7.94	3.49	1.0 M $NaNO_3$	12
Rh	6.34	8.24	1.90	4.47	7.91	3.44	1.0 M $NaClO_4$	5,13
Ir	6.29	8.10	1.81	4.80	7.86	3.06	1.0 M NaCl	This work

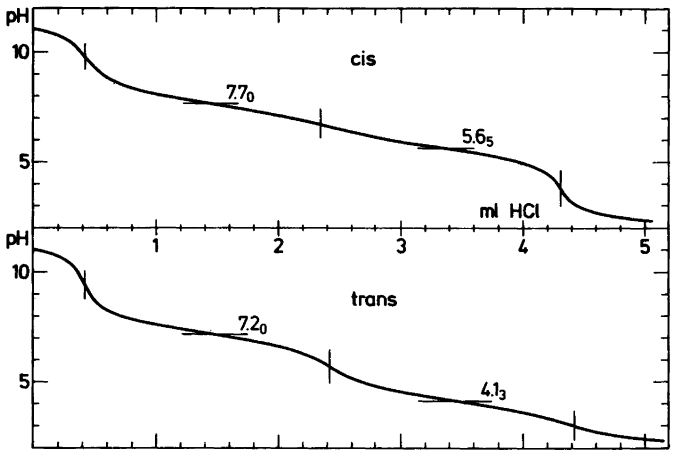

Fig. 3. Titration curves obtained by dissolution of *cis*- and *trans*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$, respectively, in an excess of 0.1 M NaOH and back titration with 0.1 M HCl.

values published by Baranovskii *et al.*[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,[14] *cis*-$[Ir(en)_2(OH)(H_2O)]S_2O_6$ on heating liberates approx. 1 mol of H_2O *per* mol of metal (Fig. 4)

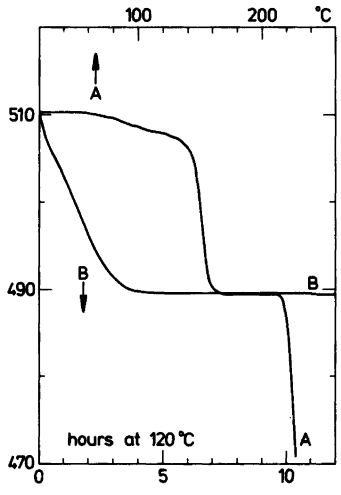

Fig. 4. Thermogravimetric analysis of *cis*-$[Ir(en)_2(OH)(H_2O)]S_2O_6$ in air. The ordinate gives a number which is proportional to the sample weight, so that the value at the plateau is 489.5 *i.e.* half the moleular weight of $[(en)_2Ir(OH)_2Ir(en)_2](S_2O_6)_2$. (A) Heating rate 2 °C/min. (B) Constant temperature 120 °C.

and forms the dimer[15] Δ,Λ-$[(en)_2Ir(OH)_2Ir(en)_2](S_2O_6)_2$. (The elemental analyses – see experimental section – show that the starting material does not contain water of crystallization). *cis*-$[Ir(en)_2(OH)(H_2O)](ClO_4)_2$ does not form a dimer on heating but starts to decompose at *ca.* 140 °C.

Acknowledgements. The authors wish to thank Dr. Ole Mønsted 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.

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Received June 29, 1983.