The Preparation, Separation and Characterization of Some Ammine Complexes of Iridium(III)

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Procedures are given for the preparation and isolation of the following compounds: *mer*-$[Ir(NH_3)_3Cl_3]$, *cis*-$[Ir(NH_3)_4Cl_2]Cl \cdot 1/2H_2O$, *trans*-$[Ir(NH_3)_4Cl_2]Cl \cdot H_2O$, $[Ir(NH_3)_5Cl]Cl_2$, *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]CF_3SO_3$ and $[Ir(NH_3)_5(OOCCH_3)](ClO_4)_2$. Furthermore, a straightforward method for the preparation of $[Ir(NH_3)_6]Cl_3$ in high yield is given. Also, the preparation of $[Ir(NH_3)_5(H_2O)](ClO_4)_3$ is described. In addition to chemical analysis the compounds have been characterized by their electronic spectra, by their reactions with neat trifluoromethanesulphonic acid (chloro species), and by their IR spectra (acetato species). The concentration acidity constant of $[Ir(NH_3)_5(H_2O)]^{3+}$ was determined to be (1.0 M $NaClO_4$): $-\log(K_a/M) =$ 6.716(7) (25 °C) and 6.323(4) (40 °C).

A survey of the literature shows that among the cationic and neutral ammine- and amminechloroiridium(III) species only the hexaammine[1–7] and pentaamminechloro[1,6–15] species have hitherto been isolated and well characterized. Tetraamminedichloro species (probably the *trans*-isomer) have been mentioned[1,12–18] but Ford *et al.*[19] were the first to assign the *trans*-isomer. Species of the empirical formula $Ir(NH_3)_3Cl_3$ have been mentioned,[1,12,15,17,18,20] but this formula may well have referred to compounds such as $[Ir(NH_3)_6][IrCl_6]$, $[Ir(NH_3)_5Cl]_3[IrCl_6]_2$, and $[Ir(NH_3)_4Cl_2]_3[IrCl_6]$.

In the present paper we describe a procedure which yields *mer*-$[Ir(NH_3)_3Cl_3]$, *cis*- and *trans*-$[Ir(NH_3)_4Cl_2]^+$ and $[Ir(NH_3)_5Cl]^{2+}$, together with a modification of this procedure which, in addition to these, also yields *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]^+$ and $[Ir(NH_3)_5(OOCCH_3)]^{2+}$. Furthermore, a straightforward method for the preparation of $[Ir(NH_3)_6]Cl_3$ in high yield is given. Also the preparation of $[Ir(NH_3)_5(H_2O)](ClO_4)_3$ is described. Attempts to prepare *cis*- and *trans*-$[Ir(NH_3)_4Cl_2]^+$ by a method similar to that used for the analogous 1,2-ethanediamine complexes,[21] i.e. refluxing of a solution of $IrCl_3 \cdot aq$ acidified with acetic acid for several hours with slow addition of the ligand, did not give reproducible results owing to the volatility of ammonia, and the ammonia was therefore provided by acid hydrolysis of urea. Such reaction of an aqueous solution of $IrCl_3 \cdot aq$ and acetic acid with urea results, however, in a great variety of species. After the reaction mixture had been evaporated to dryness, the residue heated to 150 °C for 12 h, the remanent leached with water and polymeric material removed by passing the solution through a short column of SP-Sephadex C-25 cation exchanger, one or two neutral and at least eleven cationic species can be detected by chromatography on an FPLC (fast protein liquid chromatography) instrument (Fig. 1a).

If the solution is acidified with HCl and refluxed for 2 h, after which the solution is evaporated to dryness and the remanent washed with ethanol and dissolved in water, the chromatogram of this solution looks simpler, as shown in Fig. 1b; furthermore, the amounts of *mer*-$[Ir(NH_3)_3Cl_3]$, $[Ir(NH_3)_4Cl_2]^+$ and $[Ir(NH_3)_5Cl]^{2+}$ have increased relative to the remaining species. For identification of some of the bands Fig. 1c shows the chromatogram of a mixture of *mer*-$[Ir(NH_3)_3Cl_3]$ (1), *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]^+$ (2), *trans*-$[Ir(NH_3)_4Cl_2]^+$ (3), *cis*-$[Ir(NH_3)_4Cl_2]^+$ (4), $[Ir(NH_3)_5(OOCCH_3)]^{2+}$ (5) and $[Ir(NH_3)_5Cl]^{2+}$ (6).

Experimental

Materials. Iridium(III) chloride hydrate (ca. 3.1 H_2O/mol Ir) was obtained from Johnson, Matthey and Co. All other chemicals were of analytical or reagent grade and were used without further purification.

Instrumentation. Absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer after the solutions had been filtered through Millipore filters no. HAWPO1300, 0.45 μm. The purity of the products was checked by chromatography on a Pharmacia FPLC instrument equipped with a Mono S cation-exchange column. 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.

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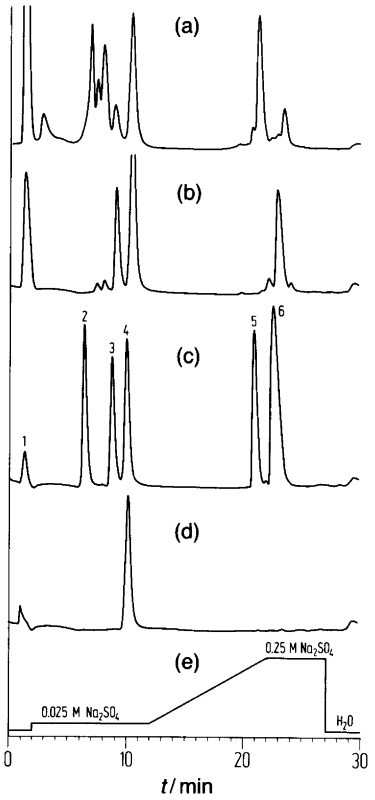

Fig. 1. Analytical separations by ion-exchange chromatography on a Pharmacia FPLC instrument equipped with a Mono S cation-exchange column. Detection wavelength: 254 nm. Flow rate: 0.8 ml/min. (a) The filtered reaction mixture. See synthetic procedure 6. (b) The solution obtained after treatment of the reaction mixture shown in (a) with HCl. See synthetic procedure 1. (c) A solution of *mer*-$[Ir(NH_3)_3Cl_3]$ (1), *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]CF_3SO_3$ (2), *trans*-$[Ir(NH_3)_4Cl_2]Cl \cdot H_2O$ (3), *cis*-$[Ir(NH_3)_4Cl_2]Cl \cdot \frac{1}{2}H_2O$ (4), $[Ir(NH_3)_5(OOCCH_3)](ClO_4)_2$ (5) and $[Ir(NH_3)_5Cl]Cl_2$ (6). (d) A solution of *cis*-$[Ir(NH_3)_4Cl_2]Cl \cdot \frac{1}{2}H_2O$. The peak after 1 min is probably an artifact caused during the injection of the sample. It occurs on all the chromatograms of the pure compounds. (e) The elution profile used in all cases: water for 2 min, 0.025 M Na_2SO_4 for 10 min, linear gradient from 0.025 to 0.25 M Na_2SO_4 during 10 min, 0.25 M Na_2SO_4 for 5 min, and finally water for 3 min.

Synthetic Procedures

1. *$[Ir(NH_3)_5Cl]Cl_2$*, cis- *and* trans-*$[Ir(NH_3)_4Cl_2]Cl$ and* mer-*$[Ir(NH_3)_3Cl_3]$*. In a 500 ml round bottomed flask fitted with a condenser a mixture of 2.66 g of $IrCl_3 \cdot 3.1\ H_2O$ (7.51 mmol), 1.25 g of acetic acid (20.8 mmol) and 250 ml of water were refluxed with magnetic stirring. After complete dissolution of the iridium chloride (ca. 20 min) 0.68 g of urea (11.3 mmol) was added to the red-brownish solution and the mixture was refluxed for 2 h. Another 0.68 g of urea (11.3 mmol) was added to the now orange solution and refluxing was continued for a further 3 h, after which the light orange solution was allowed to cool to room temperature. The reaction mixture was evaporated to dryness on a rotating vacuum evaporator, RVE, (final bath temperature 90 °C) and the flask containing the light brown residue was heated to 150 °C for 12 h. To the remanent was added 500 ml of water and the mixture was heated to boiling. 1.0 g of SP-Sephadex C-25 (Li^+-form) was then added and the hot mixture was filtered through a short column containing 1.0 g of SP-Sephadex C-25 (Li^+-form). The column was washed with 100 ml of 0.1 M LiCl and the yellow filtrate and eluate (alternatively this solution was used for procedure 6) were evaporated to a volume of ca. 250 ml on an RVE (final bath temperature 60 °C). To the solution was added 250 ml of 12 M HCl and the mixture was refluxed for 2 h, during which time white crystals of $[Ir(NH_3)_5Cl]Cl_2$ precipitated. The solution was then cooled to room temperature and evaporated to dryness on a RVE (final bath temperature 60 °C). The residue was extracted with hot ethanol and the suspension was filtered, washed with ethanol and then ether and dried in air.

The product was extracted on the filter with 3×50 ml of 50 °C hot water, leaving ca. 0.4 g of crude *mer*-$[Ir(NH_3)_3Cl_3]$ which was washed with ethanol and then ether and dried in air. The filtrate was diluted to a volume of 400 ml (Fig. 1b), and applied on a column of 40 g of SP-Sephadex C-25 (Li^+-form, ca. 50 cm long and ca. 2.5 cm in diameter) which was then washed with water until the eluate was colourless (ca. 400 ml): Fraction I {containing the orange *mer*-$[Ir(NH_3)_3Cl_3]$}. The column was then eluted with 0.1 M LiCl. The yellow band separated into two which were collected separately. After elution with ca. 800 ml the first, dark yellow, band containing the *trans*-isomer was collected (ca. 150 ml). The second, lemon yellow, band containing the *cis*-isomer was collected in the next ca. 150 ml of eluent. The two fractions were evaporated to dryness on an RVE (final bath temperature 60 °C). LiCl was extracted with ethanol and the crystals were filtered, washed with ethanol and then ether, and dried in air. Yield: 0.28 g (10 %) of *trans*-$[Ir(NH_3)_4Cl_2]Cl$ and 0.54 g (20 %) of *cis*-$[Ir(NH_3)_4Cl_2]Cl$.

The Sephadex from the short column and from the top of the long column containing some dark polymeric materials was washed with ethanol and then ether, and dried in air. The Sephadex was burned in a crucible. After the residue had been washed with water and dried in air 0.32 g (22 %) of Ir were recovered.

The pale yellow band near the top of the column contained $[Ir(NH_3)_5Cl]^{2+}$, the chloride of which is sparingly soluble. The Sephadex containing pentaammine was therefore transferred to a sintered glass filter and extracted with 4×25 ml of boiling aqueous 2 M LiCl by stirring for a few seconds followed by filtration. The collected filtrates were allowed to stand for crystallization first at room temperature then overnight in a refrigerator. The crystals were filtered, washed with ethanol and then ether, and dried in air. Yield: 0.48 g (17 %) of pale yellow $[Ir(NH_3)_5Cl]Cl_2$. (Found: H 3.89; N 18.32; Cl 27.66. Calc. for $IrH_{15}N_5Cl_3$: H 3.94; N 18.25; Cl 27.72).

The 0.4 g of crude *mer*-$[Ir(NH_3)_3Cl_3]$ were extracted with 200 ml of boiling water and the mixture was filtered through 2 g of SP-Sephadex C-25 which were then washed

with 25 ml of water. The filtrate was mixed with fraction I. The mixture was evaporated on an RVE to a volume of 200 ml, and then boiled in order to dissolve the precipitate. The solution was filtered and allowed to stand for crystallization, first at room temperature, then in a refrigerator overnight. The crystals were filtered and washed first with water, then with ethanol and finally with ether, and dried in air. Yield: 0.55 g (21 %) of orange *mer*-$[Ir(NH_3)_3Cl_3]$. (Found: H 2.59; N 11.98; Cl 30.27. Calc. for $IrH_9N_3Cl_3$: H 2.59; N 12.02; Cl 30.42).

2. trans-*$[Ir(NH_3)_4Cl_2]Cl \cdot H_2O$*. A 1.0 g sample of *trans*-$[Ir(NH_3)_4Cl_2]Cl$ was dissolved in 10 ml of water by heating and the solution was filtered on a preheated filter and allowed to stand for crystallization, first at room temperature then overnight in a refrigerator. The crystals were filtered, washed with 2 ml of ice-cold water, then with ethanol and finally with ether, and dried in air. Yield: 0.78 g (74 %) of yellow *trans*-$[Ir(NH_3)_4Cl_2]Cl \cdot H_2O$. (Found: H 3.59; N 14.61; Cl 27.58. Calc. for $IrH_{14}N_4Cl_3O$: H 3.67; N 14.56; Cl 27.65).

3. trans-*$[Ir(NH_3)_4Cl_2]ClO_4 \cdot H_2O$*. The mother liquor and wash water from the recrystallization of the chloride were heated to boiling and 4 ml of 70 % $HClO_4$ were added. The solution was allowed to stand for crystallization, first at room temperature and then overnight in a refrigerator. The crystals were filtered, washed with ethanol and then ether, and dried in air. Yield: 0.07 g (6 %) of *trans*-$[Ir(NH_3)_4Cl_2]ClO_4 \cdot H_2O$. (Found: H 2.94; N 12.59; Cl 23.20. Calc. for $IrH_{14}N_4Cl_3O_5$: H 3.14; N 12.49; Cl 23.70).

4. cis-*$[Ir(NH_3)_4Cl_2]Cl \cdot \frac{1}{2}H_2O$*. A 1.0 g sample of *cis*-$[Ir(NH_3)_4Cl_2]Cl$ was dissolved in 7 ml of water by heating and the solution was filtered and allowed to stand for crystallization, first at room temperature and then overnight in a refrigerator. The crystals were filtered, washed with 2 ml of ice-cold water, then with ethanol and finally with ether, and dried in air. Yield: 0.71 g (69 %) of lemon-yellow *cis*-$[Ir(NH_3)_4Cl_2]Cl \cdot \frac{1}{2}H_2O$. (Found: H 3.54; N 14.91; Cl 27.95. Calc. for $IrH_{13}N_4Cl_3O_{0.5}$: H 3.49; N 14.91; Cl 28.31).

5. cis-*$[Ir(NH_3)_4Cl_2]ClO_4 \cdot \frac{1}{2}H_2O$*. The mother liquor and wash water from the recrystallization of the chloride were heated to boiling and 4 ml of 70 % $HClO_4$ were added. The solution was allowed to stand for crystallization, first at room temperature and then overnight in a refrigerator. The crystals were filtered, washed with ethanol and then ether, and dried in air. Yield: 0.22 g (18 %) of *cis*-$[Ir(NH_3)_4Cl_2]ClO_4 \cdot \frac{1}{2}H_2O$. (Found: H 2.90; N 12.78; Cl 23.32. Calc. for $IrH_{13}N_4Cl_3O_{4.5}$: H 2.98; N 12.74; Cl 24.19).

6. trans-*$[Ir(NH_3)_4(OOCCH_3)Cl]CF_3SO_3$ and $[Ir(NH_3)_5(OOCCH_3)](ClO_4)_2$*. If the eluate from the short Sephadex column (see procedure 1) was *not* refluxed with HCl these two salts could also be isolated. The eluate was evaporated to dryness on an RVE. The residue was extracted with hot ethanol. The suspension was filtered, and the remainder washed with ethanol and ether and dried in air. The product was extracted on the filter with 3×50 ml of 50 °C hot water, leaving ca. 0.2 g of crude *mer*-$[Ir(NH_3)_3Cl_3]$. The filtrate was diluted to a volume of 400 ml, applied on the long column used in procedure 1 and the column washed with 400 ml of water. *mer*-$[Ir(NH_3)_3Cl_3]$, 0.35 g (13 %) was isolated as described earlier.

The column was then eluted with 0.1 M LiCl. After the first ca. 300 ml the top band (ca. 7 cm) was removed and extracted with boiling 2 M LiCl as in procedure 1. 0.15 g (5 %) of $[Ir(NH_3)_5Cl]Cl_2$ were isolated. The mother liquor was evaporated to dryness on an RVE. The residue was extracted with hot ethanol, the suspension was filtered, and the remainder washed with ethanol and ether and dried in air. Yield: 0.40 g (13 %) of $[Ir(NH_3)_5(OOCCH_3)]Cl_2$. The product was dissolved in 3.5 ml of hot water and the solution was filtered. The filtrate was heated to boiling point. Addition of 3.5 ml of a saturated solution of $NaClO_4$ resulted in a copious precipitate. The mixture was left overnight in a refrigerator before the crystals were filtered, washed with ethanol and ether, and dried in air. Yield: 0.35 g (9 %) of white $[Ir(NH_3)_5(OOCCH_3)](ClO_4)_2$. (Found: C 4.24; H 3.23; N 12.91; Cl 13.42. Calc. for $IrC_2H_{18}N_5Cl_2O_{10}$: C 4.49; H 3.39; N 13.08; Cl 13.25).

The elution of the column was continued. The next ca. 400 ml of eluate were discharged. Then the faintly yellow band containing *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]^+$ was collected in the next ca. 150 ml of eluate, *trans*-$[Ir(NH_3)_4Cl_2]^+$ in the following ca. 250 ml and *cis*-$[Ir(NH_3)_4Cl_2]^+$ in the next ca. 250 ml. The three fractions were evaporated to dryness and the residues extracted with ethanol etc. The yields were: 0.15 g (5 %) of *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]Cl$, 0.20 g (7 %) of *trans*-$[Ir(NH_3)_4Cl_2]Cl$ and 0.45 g (16 %) of *cis*-$[Ir(NH_3)_4Cl_2]Cl$. The dichloro species were recrystallized as described earlier. The 0.15 g of acetatochloro complex were dissolved in 0.3 ml of water and the solution was filtered. 0.3 ml of a saturated solution of $NaCF_3SO_3 \cdot H_2O$ were added to the filtrate. The mixture was heated to boiling and allowed to stand for crystallization, first at room temperature and then in a refrigerator overnight. The crystals were filtered, washed with ethanol and ether, and dried in air. Yield 0.10 g (3 %) of canary yellow needles of *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]CF_3SO_3$. (Found: C 6.76; H 2.99; N 11.13; S 6.37; Cl 7.54. Calc. for $IrC_3H_{15}N_4ClF_3SO_3$: C 7.15; H 3.00; N 11.12; S 6.36; Cl 7.04).

7. *$[Ir(NH_3)_6]Cl_3$*. 3.04 g (8.58 mmol) of $IrCl_3 \cdot 3.1H_2O$ (or an equivalent amount of *mer*-$[Ir(NH_3)_3Cl_3]$ or $[Ir(NH_3)_5Cl]Cl_2$) were placed in a Teflon container and 50 ml of 12 M ammonia were added. The container was closed and placed in an autoclave containing ammonia solution for pressure equilibration. The autoclave was closed and heated to 150 °C for 96 h. The resulting pale

yellow solution was filtered and the filtrate evaporated to dryness on a RVE (final bath temperature 50 °C). The white residue was extracted on a sintered glass filter with 4×5 ml of 4 M HCl* and the remainder washed with ethanol and then ether, and dried in air. The crude product (3.10 g) was dissolved in 20 ml of boiling water. The solution was filtered and 10 ml of 12 M HCl were added to the filtrate. The mixture was allowed to stand for crystallization, first at room temperature and then overnight in a refrigerator. The crystals were filtered, washed thoroughly with 96 % ethanol and then with ether, and dried in air. Yield: 2.90 g (84 %) of white $[Ir(NH_3)_6]Cl_3$. (Found: H 4.49; N 21.18; Cl 26.97. Calc. for $IrH_{18}N_6Cl_3$: H 4.53; N 20.97; Cl 26.54).

8. *$[Ir(NH_3)_5(H_2O)](ClO_4)_3$*. This compound was prepared by a slight modification of the method of Schmidtke[14] and Palmaer:[1] 0.80 g (2.08 mmol) of $[Ir(NH_3)_5Cl]Cl_2$ was dissolved in 50 ml of 1 M NaOH and the solution was refluxed for 3 h, during which the colour changed from pale yellow to colourless. The solution was cooled in ice and 10 ml of ice-cold 70 % $HClO_4$ were added dropwise with cooling and stirring at a rate such that the temperature did not exceed 5 °C. After cooling for a further 1 h the precipitate was filtered, washed, first with 2×5 ml of 1 M $HClO_4$, then with ethanol and finally with ether, and dried in air. The crude product (1.15 g) was dissolved in 10 ml of boiling water and the solution was filtered. 10 ml of boiling 1 M $HClO_4$ were added to the filtrate and the mixture was left for crystallization, first at room temperature, and then overnight in a refrigerator. The crystals were filtered, washed, first with 2×5 ml of 1 M $HClO_4$, then with 96 % ethanol and finally with ether, and dried in air. Yield: 1.10 g (89 %) of white $[Ir(NH_3)_5(H_2O)](ClO_4)_3$. (Found: H 2.87; N 11.36; Cl 17.79. Calc. for $IrH_{17}N_5Cl_3O_{13}$: H 2.89; N 11.80; Cl 17.91).

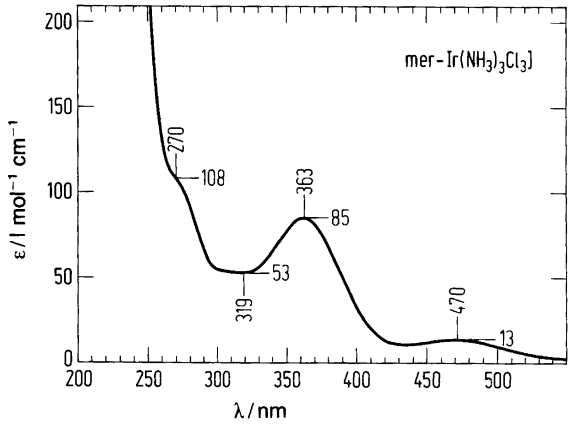

Fig. 2. The absorption spectrum of *mer*-$[Ir(NH_3)_3Cl_3]$. The value of the absorptivity should be taken with some reservation, because the low solubility and the low rate of dissolution required the solution to be prepared by boiling the compound with 1 M LiCl followed by filtration. The spectrum was recorded at ca. 80 °C.

* A small amount, ca. 0.06 g, of $[Ir(NH_3)_5Cl]Cl_2$ could be recovered by heating the filtrate to boiling point for a few minutes followed by cooling and filtration.

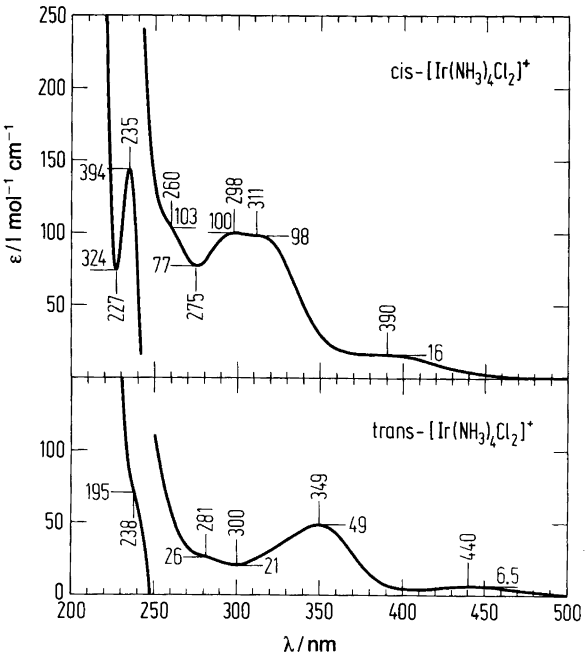

Fig. 3. The absorption spectra of *cis*-$[Ir(NH_3)_4Cl_2]Cl \cdot \frac{1}{2}H_2O$ and *trans*-$[Ir(NH_3)_4Cl_2]Cl \cdot H_2O$.

Results and discussion

The absorption spectrum of *mer*-$[Ir(NH_3)_3Cl_3]$ is shown in Fig. 2. The compound is assigned as the meridional geometrical isomer by a comparison of the absorption spectrum with that of the analogous compound $[Ir(en)(enH)Cl_3]Cl \cdot H_2O$ (en = 1,2-ethanediamine; enH^+ = 2-aminoethylammonium ion),[21] the crystal structure of which has been determined by X-ray diffraction.[22] The absorption spectra of *cis*- and *trans*-$[Ir(NH_3)_4Cl_2]^+$ are shown in Fig. 3. The assignments of the geometrical isomers are made by comparison of the spectra with those of the analogous 1,2-ethanediamine complexes[21] and by the reactions with neat trifluoromethanesulphonic acid, triflic acid. In the *cis*-isomer both of the chloride ligands can be replaced by triflate ions; in the *trans*-isomer only one can. This is in agreement with the experimental observation[23] that the *trans*-labilizing effect of the triflate ion is so low that if two chloride ions are *trans* to each other, only one of them will be replaced by $CF_3SO_3^-$ on heating with neat triflic acid. The base hydrolysis of these two species is presently being studied.[24]

In Fig. 4 the absorption spectrum of $[Ir(NH_3)_5Cl]^{2+}$ is shown. The maxima are in reasonable accordance with the results published by Jørgensen[9] [λ_{max} (ε_{max})]: [360(10); 286(71)], Blanchard and Mason[11] [362(9.5); 287(72); 226(370)] and Schmidtke[10,14] [286(73); 227(333)]. Fig. 4 also

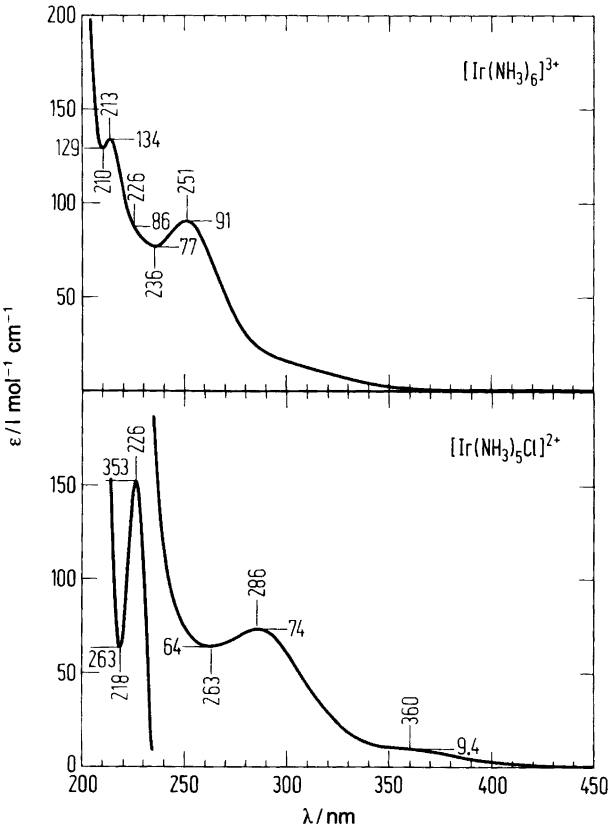

Fig. 4. The absorption spectra of $[Ir(NH_3)_6]Cl_3$ and $[Ir(NH_3)_5Cl]Cl_2$.

shows the absorption spectrum of $[Ir(NH_3)_6]^{3+}$. It is in reasonable accordance with the results published by Schmidtke[3] [λ_{max} (ε_{max})]: [315(14); 251(92); 214(160)]. Schmidtke assigns the transition at 214 nm as $^1A_{1g} \rightarrow {}^1T_{2g}$. This assignment may be disputable, however. It is well known that the second spin-allowed transition of the hexaammine complexes of Cr(III), Co(III) and Rh(III) all exhibit a lower absorbance than that of the first spin-allowed band.[9] The assignment of the transition at 214 nm as $^1A_{1g} \rightarrow {}^1T_{2g}$ also results in an exceptional high value of the Racah parameter B,[25] which means that in the nephelauxetic series[26] certain ligands, i.e. NH_3 and H_2O, should be interchanged when coordinated in an iridium(III) complex. In the spectrum of $[Ir(NH_3)_6]^{3+}$ (Fig. 4) it is possible to see a shoulder around 226 nm. It is probably more acceptable to assign this shoulder to the transition $^1A_{1g} \rightarrow {}^1T_{2g}$, since this assignment would give a reasonable value of the B-parameter, which fits the nephelauxetic series. In the absorption spectra of $[Ir(en)_3]^{3+}$ (Ref. 27) and $[Ir(NH_3)_5(H_2O)]^{3+}$ (Fig. 5) a similar shoulder is observed around the same value, which in these complexes undoubtedly can be assigned as the transition $^1A_{1g} \rightarrow {}^1T_{2g}$. It is also interesting to notice that the absorption spectra of these two complexes both exhibit a third transition at higher energy, 206 and 212 nm, respectively, which corresponds to the band at 213 nm in the spectrum of $[Ir(NH_3)_6]^{3+}$. With this assignment of shoulders to represent the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition, many spectra can be interpreted quantitatively by using the usual ligand-field scheme. We have to admit, however, that we have no clue to the assignment of the conspicuous neighbour to the transition we have assigned as $^1A_{1g} \rightarrow {}^1T_{2g}$; we only make the comment that it seems too narrow to represent a ligand-field transition. From a theoretical point of view further studies of this

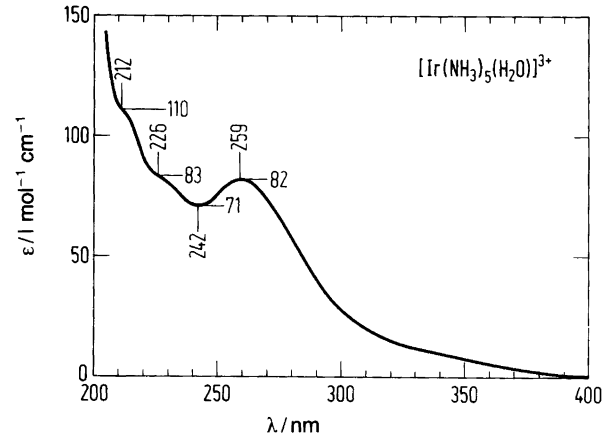

Fig. 5. The absorption spectrum of $[Ir(NH_3)_5(H_2O)](ClO_4)_3$ dissolved in 0.1 M $HClO_4$.

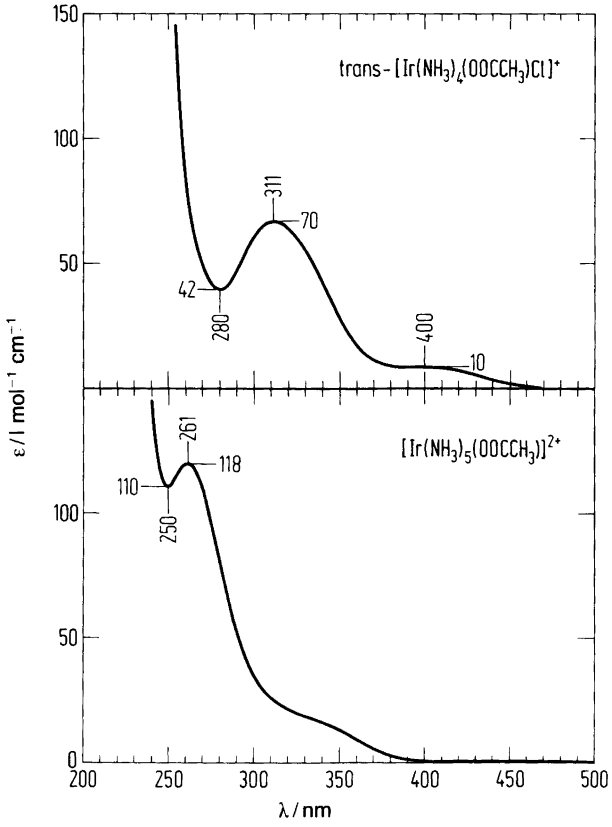

Fig. 6. The absorption spectra of *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]CF_3SO_3$ and $[Ir(NH_3)_5(OOCCH_3)](ClO_4)_2$.

third transition, which is observed in the iridium(III) ammine and amine complexes, would be of interest.

The absorption spectrum of $[Ir(NH_3)_5(H_2O)](ClO_4)_3$ is shown in Fig. 5. It is in reasonable accordance with that published by Schmidtke,[10] [λ_{max} (ε_{max})]: [333(12)sh; 258(86); 213(128)] and by Palmer and Harris:[28] [258(87)], [λ_{min} (ε_{min})]: [242(75)]. The concentration acidity constant of $[Ir(NH_3)_5(H_2O)](ClO_4)_3$ was determined by regression analysis as described by Mønsted and Mønsted[29] of the titration data from dissolution in an excess of $HClO_4$ and back-titration with NaOH. The results are (1.0 M $NaClO_4$): $-\log(K_a/M) = 6.716(7)$ (25 °C) and 6.323(4) (40 °C). This is in good agreement with the value estimated by Borghi and Monacelli.[30]

The absorption spectra of *trans*-$[Ir(NH_3)_4(OOCCH_3)Cl]^+$ and $[Ir(NH_3)_5(OOCCH_3)]^{2+}$ are shown in Fig. 6. The former is assigned as the *trans*-isomer as it is converted into *trans*-$[Ir(NH_3)_4Cl_2]^+$ on heating in 1 M HCl. The IR spectra of both of the two compounds exhibit bands attributable to the acetate group,[31] viz. 940 cm^{-1} (ν_{C-CH}), 1400 cm^{-1} [$\nu_{sym}(CO_2)$], 635 cm^{-1} (COO bending), and ca. 1600 cm^{-1} [$\nu_{as}(CO_2)$]. The hydrolysis of the acetatopentaammine ion has been studied by Monacelli *et al.*,[32] who do not publish other characteristics of the compound.

The purity of the products was checked by chromatography. In Fig. 1d the chromatogram for *cis*-$[Ir(NH_3)_4Cl_2]Cl \cdot \frac{1}{2}H_2O$ is shown as an example.

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