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# Synthesis of rhodium(III)–pyridine complexes: an electrophoretic and chromatographic study

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**Abstract**

The synthetic methods for the preparation of rhodium(III)–pyridine complexes were examined using zone electrophoresis and thin-layer chromatography. Most syntheses produce a mixture of three to four complexes. Fresh solutions of commercial $RhCl_3 \cdot nH_2O$ contain as many as ten electrophoretically different species. A yellow electrophoretically pure $Rh(py)_3Cl_3$ (presumably the fac form) could be prepared, which in dilute acid converts into another neutral species, presumably the mer form. These could be separated by thin-layer chromatography on cellulose. The importance of examining the purity of monodentate complexes prepared by the usual synthetic methods is stressed.

*Keywords:* Rhodium(III); Pyridine

## 1. Introduction

Electrophoretic and chromatographic studies have demonstrated that metal complexes with monodentate ligands usually form, in solution, mixtures with one or more ligand groups attached to the metal [1]. A typical case is the solution of Rh(III) in aqueous solutions of HCl which varies with HCl concentration, age and temperature but always contains several species which are sufficiently stable to permit their separation providing the separation method is sufficiently fast. Isolation of a single species from such solutions is often difficult as interconversion occurs with time, with heating, and with a change in ligand concentration. In spite of this, some authors succeeded in measuring absorption spectra or even isolated solids by paying attention to the time factor and the labile character of the complexes.

The kinetics of the hydrolysis of halide complexes have been studied extensively in the last 40 years or so and have contributed to the understanding of the nature of monodentate ligand complexes.

We noted, however, that these concepts were not generally applied when complexes were synthesised. The origin of this study stems from the work of the solution chemistry of Rh(III) carried out about 40 years ago at the Institut de Radium, Paris [2]. $Rh(py)_3Cl_3$ (py=pyridine) was prepared using the method of Collman and Holtzclaw [3], and the mother liquor was examined by paper electrophoresis with a simple glass plate technique (250 V for 45 min with 0.1 *M* KCl as electrolyte). This yielded four well-separated bands (one cationic, one neutral, two anionic). The crystallised product was assumed to be $Rh(py)_3Cl_3$.

This work was taken up again recently. A chromatogram of the mother liquor yielded 8 spots by eluting with butanol/2.4 *M* HCl, and so did the

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crystals of supposed $Rh(py)_3Cl_3$. Fac-mer isomers cannot be separated in an electrophoretic separation.

It was thus decided to examine the published syntheses of Rh(III) pyridine complexes. The reactions employed usually did not yield a single species. Most gave the entire spectrum of Rh(III) chloropyridino complexes.

The work described here is intended to be an extension to the literature on the preparation of these complexes, which were often considered to yield essentially pure compounds.

## 2. Experimental

### 2.1. Materials

$RhCl_3 \cdot nH_2O$ was obtained from Johnson Matthey and Brandenberger (Zurich, Switzerland). All other compounds were obtained from Fluka (Buchs, Switzerland).

### 2.2. Electrophoresis and chromatography

Electrophoresis was performed on a Multiphor II Electrophoresis system with cooling table (Pharmacia Biotech, Uppsala, Sweden) powered by an EPS 3500 electrophoresis power supply using Whatman 3MM (Whatman International, Maidstone, England) paper strips as support. The solid samples were dissolved in 0.12 *M* HCl (sometimes a few drops of acetone were added to help dissolution) and electrophorised immediately to prevent hydrolysis reactions. The paper strips were impregnated with the electrolyte, dried with adsorbant paper, and the sample was applied in a thin line using cut-off melting point capillaries. The electrolyte used throughout was 0.12 *M* HCl. The electropherograms were then revealed using a 2% $SnCl_2$ solution in 6 *M* HCl with added KI.

Thin layers used were Macherey Nagel (Düren, Germany) Cel 300 native cellulose thin layers. Standard ascending chromatography techniques were used.

### 2.3. Elemental analysis

Elemental analysis was performed by Analytische Laboratorien, Lindlar, Germany.

### 2.4. Syntheses

#### 2.4.1. $Na_3RhCl_6$

$RhCl_3 \cdot nH_2O$ (1 g), dissolved in 2 *M* HCl (10 ml), was heated in a water bath for 30 min. NaCl (0.75 g) dissolved in $H_2O$, was added, the solution was then heated with stirring at 95°C for 1 h, then evaporated to dryness. The solid obtained was recrystallised from 2 *M* HCl and EtOH at 3°C.

Purple crystals (A) were obtained and washed with EtOH and $Et_2O$, $Na_3RhCl_6 \cdot 12H_2O$ (1.78 g, 78% yield).

#### 2.4.2. $pyH[Rh(py)_2Cl_4]$ (Ref. [4])

$Na_3RhCl_6 \cdot 12H_2O$ (0.5 g) was dissolved in $H_2O$ (20 ml) and kept at 10°C. Pyridine (0.40 ml) and 37% HCl (0.14 ml) were added. The solution was stirred 10 days. After filtration 0.35 g of a pink–red solid (B) was collected (87% yield).

#### 2.4.3. $Rh(py)_3Cl_3$ (Ref. [3])

Pyridine (0.92 ml) was added to $RhCl_3 \cdot nH_2O$ (0.5 g) dissolved in $H_2O$ (6 ml). After stirring for 72 h at room temperature, a red–orange solid was formed, while the solution turned orange. This mixture was heated at 55°C for 8 h on a water bath. The solution was filtered while warm to obtain 0.26 g of an orange solid (C) (31% yield).

#### 2.4.4. $Rh(pyCH_3)_3Cl_3$

4-Picoline (0.25 ml) was added to $Na_3RhCl_6 \cdot 12H_2O$ (0.5 g) dissolved in $H_2O$ (5 ml). After stirring for 72 h at room temperature, a red–orange solid was formed, while the solution turned orange. This mixture was heated at 55°C for 8 h on a water bath. The solution was filtered while warm to obtain 0.22 g of an orange solid (D) (54% yield).

#### 2.4.5. $[Rh(py)_4Cl_2]Cl \cdot 4H_2O$ (Ref. [3])

$RhCl_3 \cdot nH_2O$ (0.4 g) was dissolved in EtOH (50 ml). Pyridine (2.1 ml) was added to the red solution. A red precipitate was formed. The mixture was refluxed for 2 days. The yellow solution formed was filtered, concentrated over a waterbath at 80°C to 10 ml. Yellow–orange crystals are formed on standing at −30°C, which is then filtered and washed with cold $H_2O$ (2×1 ml) and $Et_2O$ (2×2 ml). 0.68 g of product (E) were obtained (74.9% yield).

*2.4.6. [Rh(pyCH$_3$)$_4$Cl$_2$]Cl*

$RhCl_3 \cdot nH_2O$ (0.4 g) was dissolved in EtOH (50 ml). 4-Picoline (2.1 ml) was added to the red solution. A pink–red precipitate was formed. The mixture was refluxed for 2 days. The yellow solution formed was filtered, concentrated over a waterbath at 80°C to 5 ml. A yellow solid is formed on standing at −30°C, which is then filtered and washed with cold $H_2O$ (2×1 ml) and $Et_2O$ (2×2 ml). 0.46 g of product F were obtained (46.4% yield).

*2.4.7. [Rh(py)$_4$Cl$_2$]BPh$_4$*

$[Rh(py)_4Cl_2]Cl$ (0.15 g) and a drop of $HNO_3$ (conc.) were added to $H_2O$ (15 ml), then heated to dissolve. A yellow solution was obtained. $NaBPh_4$ (87 mg) in $H_2O$ was then added. 0.164 g of a white precipitate G were formed (80.8% yield).

## 3. Results and discussion

### *3.1. The synthesis of Rh(III) pyridine complexes*

Commercial $RhCl_3 \cdot nH_2O$ dissolves readily in water or dilute acids yielding a reddish–violet solution. Both Blasius et al. [1] and one of us [5] have reported that fresh solutions yield numerous cationic and anionic bands. It is generally assumed that solid $RhCl_3$ is a polymer linked by halogen bridges and the fresh solution contains oligomers and monomers which on standing reach equilibrium with the solvent as shown by $^{103}$Rh NMR [6,7].

Fig. 1 shows a typical series of fresh solutions in $H_2O$, 0.12 HCl and in 0.1 *M* $NaClO_4$, and up to 10 bands can be seen. Some other solutions (not shown here) yielded even more bands. This should always be kept in mind when a synthesis requires that solid 'commercial $RhCl_3$' is taken as starting material. Fig. 2 shows the densitometric evaluation of the 0.1 *M* $NaClO_4$ lane.

For this reason $Na_3RhCl_6$ was used as a starting material, and as seen in Fig. 3, it seems pure.

Reaction 2 was performed with the molar proportions used by Delepine [4], but although he reported an elemental analysis consistent with $pyH[Rh(py)_2Cl_4]$, as seen on the electropherogram in Fig. 4, this is not the case. The reaction was also attempted with varying conditions and molar proportions, but in no case was the product pure. Also, no evidence was seen in the course of our investigation of the *cis* and *trans* isomers.

If the reaction is performed using the stoichiometric ratios (at low temperature), the mother liquor shows also the presence of $[Rh(py)_2Cl_4]^-$, which can be precipitated using $AsPh_4^+$ (Fig. 5). This was also confirmed by its elemental analysis (Table 1).

If the reaction is not performed for a sufficient time, there is the risk of obtaining other products. This was shown by the same reaction performed for 3 days. The elemental analysis of the product obtained by precipitating with $AsPh_4Cl$ is consistent with $AsPh_4[Rh(H_2O)_2Cl_4]$ (Table 2).

$Rh(py)_3Cl_3$ was synthesised according to the method of Collman and Holtzclaw [3]. As seen in Fig. 6, the orange crystals formed are not pure $Rh(py)_3Cl_3$ (see also Fig. 10). We can confirm that,

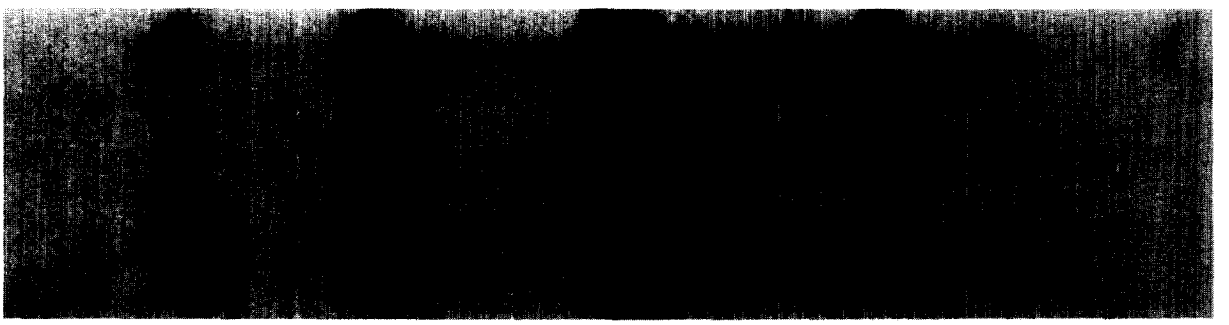


Fig. 1. Electropherogram of $RhCl_3$: A=freshly dissolved in $H_2O$; B=freshly dissolved in 0.12 *M* HCl; C=freshly dissolved in 0.1 *M* $NaClO_4$. 500 V, 97→149 mA, 20 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI (the $SnCl_2$/KI reaction colour intensity is not necessarily proportional to the concentration of analyte).

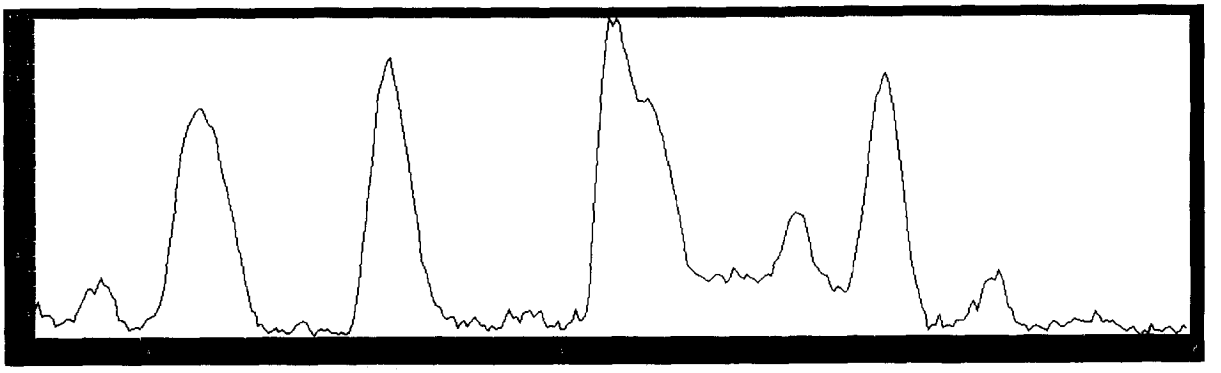


Fig. 2. Densitometric evaluation of the 0.1 *M* $NaClO_4$ lane in the above electropherogram.

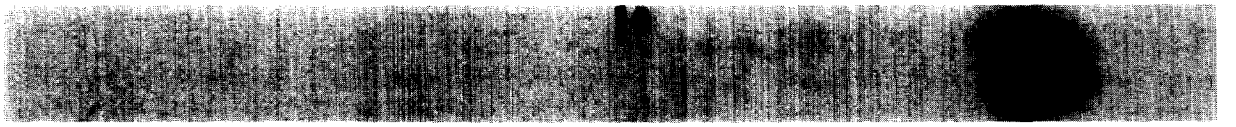


Fig. 3. Electropherogram of compound A: 500 V, 97→149 mA, 20 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

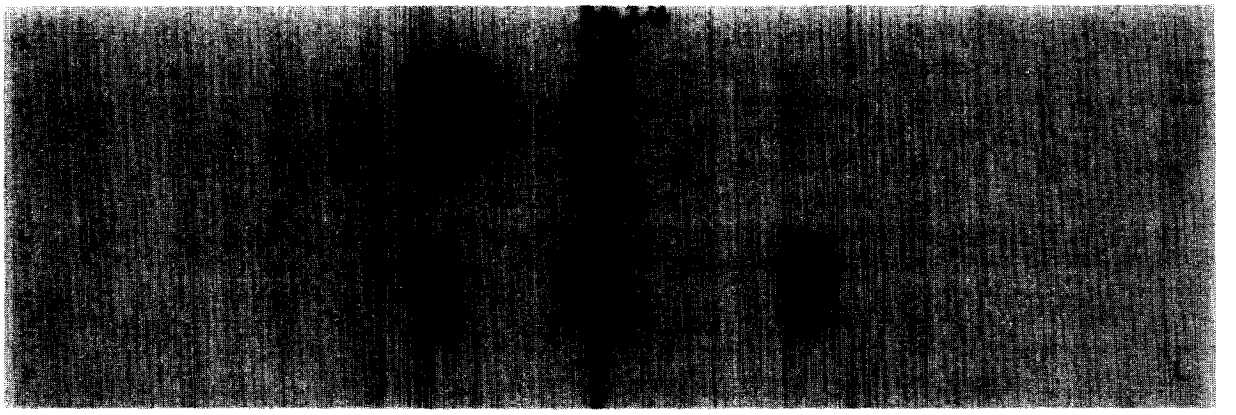


Fig. 4. Electropherogram of synthesis 2: A=mother liquor; B=compound B. 500 V, 64→118 mA, 30 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

as reported in Ref. [3], the yellow platelets formed upon standing at 4°C and at room temperature are mostly $[Rh(py)_4Cl_2]Cl$.

A variation of synthesis 3 was performed using $Na_3RhCl_6$ as starting material and using the stoichiometric ratio to produce the trichloro tripicoline-

Fig. 5. Electropherogram of synthesis 2 performed using the stoichiometric ratios. $[Rh(py)_2Cl_4]^-$ precipitated with $AsPh_4^+$: 500 V, 64→118 mA, 30 min. Revelation was done using 2% SnCl in 6 *M* HCl with added KI.

Table 1
Elemental analysis of the precipitate obtained with $AsPh_4Cl$ when the reaction is performed using the stoichiometric ratios

| $(AsPh_4[Rh(py)_2Cl_4])$ | C | H | N | Cl |
|---|---|---|---|---|
| Calculated | 51.94 | 3.85 | 3.56 | 18.04 |
| Found | 51.04 | 3.83 | 3.40 | 17.43 |

Table 2
Elemental analysis of the precipitate obtained with $AsPh_4Cl$ when the reaction is performed for 3 days using the stoichiometric ratios

| $(AsPh_4[Rh(H_2O)_2Cl_4])$ | C | H | N | Cl |
|---|---|---|---|---|
| Calculated | 43.40 | 3.64 | – | 21.35 |
| Found | 44.10 | 3.81 | 0.08 | 20.84 |

rhodium(III). From Fig. 7, it can be seen that compound D is mostly $Rh(pyCH_3)_3Cl_3$.

$(Rh(py)_4Cl_2]Cl\cdot 4H_2O$ was prepared according to the method of Collman and Holtzclaw [3]. The product obtained was pure (Fig. 8) and in good yield (75%). The synthesis of $[Rh(py)_4Cl_2]Cl$ was also reported by Cini et al. [8], who used a slightly modified procedure.

Synthesis 5 was repeated to produce the tetrapicoline compound. The yield is not as good (46%), but the product is pure (Fig. 9 and Table 3).

Compound G, $(Rh(py)_4Cl_2]BPh_4$, was synthesised to avoid the presence of a non-coordinated chloride

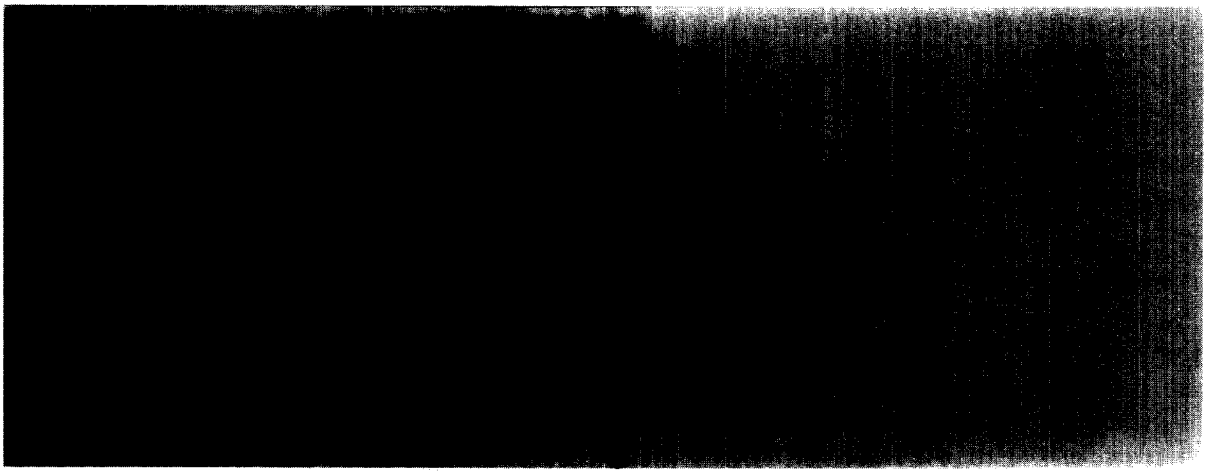


Fig. 6. Electropherogram of synthesis 3: A=mother liquor; B=washing waters; C=compound C; D=crystals formed on standing at room temperature; E=crystals formed on standing at 4°C. 500 V, 75→137 mA, 31 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

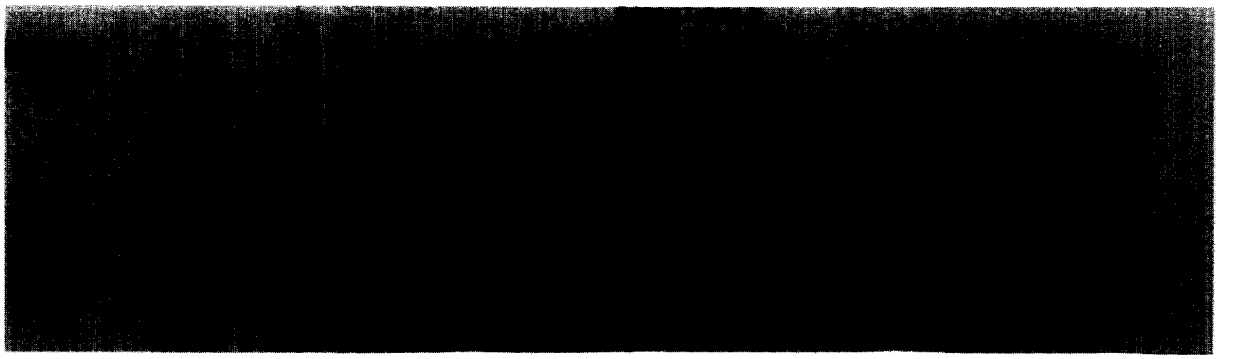


Fig. 7. Electropherogram of synthesis 4: A=mother liquor; B=compound D; C=washing waters. 500 V, 89→149 mA, 27 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

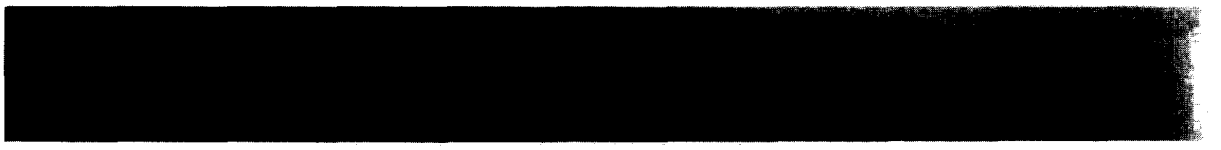


Fig. 8. Electropherogram of compound E: 500 V, 97→149 mA, 20 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

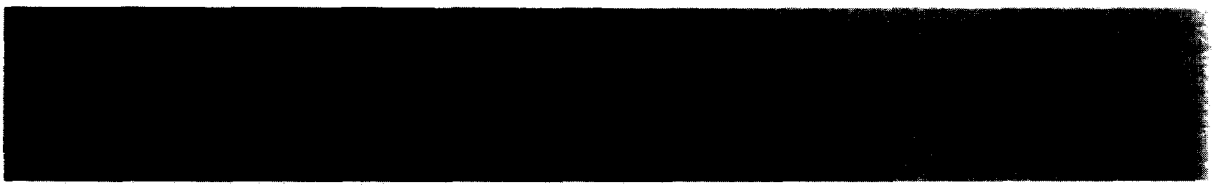


Fig. 9. Electropherogram of compound F: 500 V, 97→149 mA, 20 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

Table 3
Elemental analysis of product F

| ($[Rh(pyCH_3)_4Cl_2]Cl$) | C | H | N | Cl |
|---|---|---|---|---|
| Calculated | 49.55 | 4.85 | 9.63 | 18.28 |
| Found | 49.22 | 4.85 | 9.47 | 18.09 |

with the use of a suitable bulky counter-ion. The disadvantage in this case is the low solubility of the compound, making the electrophoresis results uncertain, although a confirmation can be obtained by elemental analysis (Table 4).

Table 4
Elemental analysis of product G

| ($[Rh(py)_4Cl_2]BPh_4$) | C | H | N | Cl |
|---|---|---|---|---|
| Calculated | 65.29 | 4.98 | 6.92 | 8.76 |
| Found | 65.27 | 4.86 | 6.87 | 8.80 |

### *3.2. $Rh(py)_3Cl_3$ isomers*

In a number of syntheses, the possibilities of forming both *cis* and *trans* $Rh(py)_2Cl_4^-$ and $Rh(py)_4Cl_2^+$ were considered, and indeed in some reactions bands, red fronts and yellow–orange rears were observed suggesting partial separations of two species with the same charge but different mobilities. Isomers of the neutral complex $Rh(py)_3Cl_3$ can obviously not be separated by electrophoresis.

$Rh(py)_3Cl_3$ was resynthesised in an analogous way to $Rh(pyCH_3)_3Cl_3$, i.e. with $Na_3RhCl_6$ as starting compound and using the stoichiometric ratios. After recrystallisation this compound was obtained electrophoretically pure (Fig. 10).

We have tried to examine such electrophoretically pure specimens by adsorption chromatography on 'native' cellulose. Fig. 11 shows that the compound when fresh (yellow) gave one band, and on standing in light gave another faster band (orange).

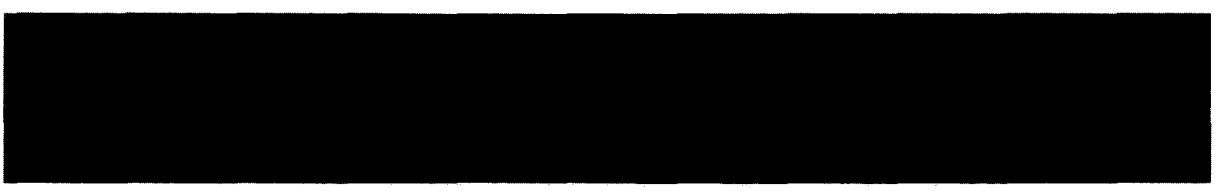


Fig. 10. Electropherogram of $Rh(py)_3Cl_3$ synthesised from $Na_3RhCl_6$ using the stoichiometric ratios: 500 V, 68→130 mA, 39 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

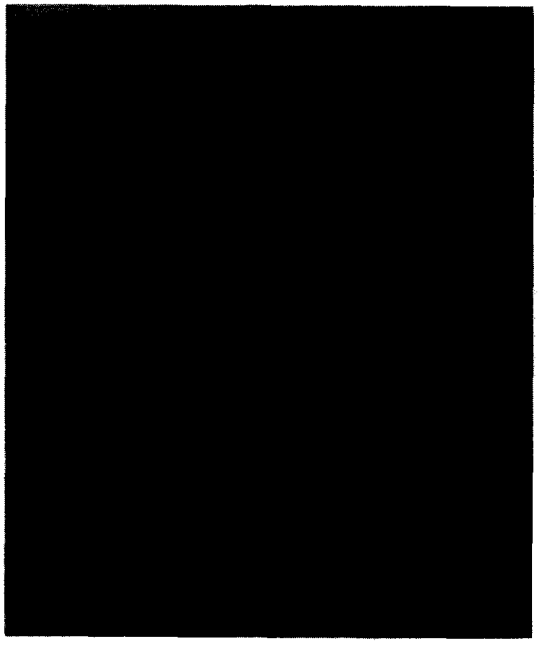


Fig. 11. Chromatogram of $Rh(py)_3Cl_3$ dissolved in 2.4 *M* HCl/acetone (50:50) after 0, 1, 2, 3 h eluted on Cel 300 thin layers with 1 *M* NaCl. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

The $R_F$ values of both bands decrease with the NaCl concentration in the eluent (Fig. 12) and thus show that they are 'salted out'.

The yellow species corresponding to the slower moving band has the same IR spectrum as that reported by Gillard and Wilkinson [9] for the *cis* (fac) isomer (1, 2, 3-$Rh(py)_3Cl_3$) (Scheme 1).

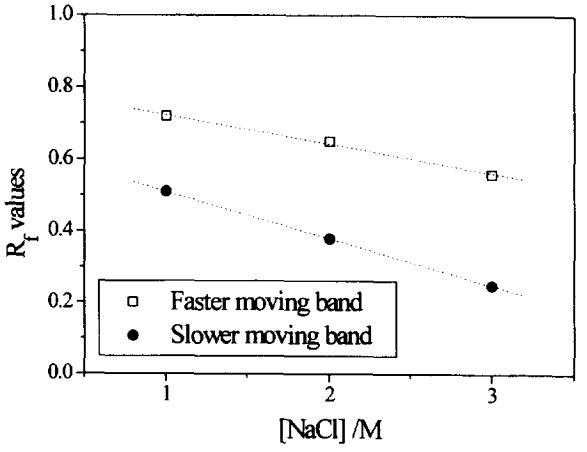
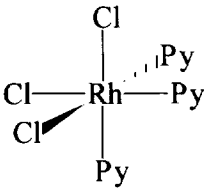



Fig. 12. Graph of $R_F$ values of the isomers of $Rh(py)_3Cl_3$ vs. [NaCl] in the eluent.




Scheme 1. 1, 2, 3-$Rh(py)_3Cl_3$.

The same solutions were electrophorised on 3MM paper strips with 0.1 *M* NaCl as electrolyte (Fig. 13).

As can be seen in Fig. 13, only neutral species are observed, and there is an increase in colour intensity with increasing time. The two species observed in the chromatogram could be the fac-mer isomers referred to by Collman and Holtzclaw [3]. It is unlikely that the one corresponding to the faster moving spot on the chromatogram, which produces a more intensily coloured complex with $SnCl_2$/KI, is a hydroxo complex as it forms in 1.2 *M* HCl. If it were an aquo replacement, the complex would be cationic, which is not the case.

## 4. Conclusion

It could be shown that almost all of the published methods for pyridine–rhodium(III) complexes yielded a multitude of constituents when subjected to electrophoresis. Even this technique is not exhaustive as, for example, it could not distinguish between the isomeric forms of $Rh(py)_3Cl_3$.

This is well known for the solution chemistry of numerous transition metals. However, it does not seem to have been appreciated in the methods of preparation of supposedly pure labile complexes.

Electrophoresis may not be suitable for the examination of other syntheses and suitable chromatographic methods may be required, however it is hoped that the results shown above, even if incomplete, illustrate the necessity to apply chromatography and electrophoresis when aiming to prepare a pure form of a complex with monodentate ligands.

Fig. 13. Electropherogram of $Rh(py)_3Cl_3$ dissolved in 2.4 *M* HCl–acetone (50:50) after 0, 1, 2, 3 h. 0.1 *M* NaCl electrolyte, 500 V, 19→29 mA, 31 min. Revelation was done using 2% $SnCl_2$ in 6 *M* HCl with added KI.

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