Use of Silver(I) Complexes in Synthesis of Bis- and Tris-[2-(arylazo)pyridine] Complexes of Ruthenium(II) and Investigation of Solid-state Isomerisation

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Efficient, new and direct synthetic routes to isomeric $[RuCl_2L_2]$ and $[RuL_3][ClO_4]_2{\cdot}H_2O$ [L = 2-(arylazo)pyridine] complexes, based on the reaction of hydrated $RuCl_3$ and $[AgL_2]ClO_4$, have been elaborated. The identity of the compounds were established from elemental analyses and spectral data. The advantages of the new methods are highlighted. Solid-state isomerisation of the dichloride complexes has been studied by different thermal methods. It is shown that two (*trans,trans* and *cis,cis*) out of the three isomers of $[RuCl_2L_2]$ are converted into the third (*trans,cis*) isomer on heating. Analyses of differential scanning calorimetry data reveal that the thermal isomerisation reactions proceed through similar intermediates. The relative thermal stabilities of the different isomers of $[RuCl_2L_2]$ are also briefly noted.

The ruthenium chemistry of 2-(arylazo)pyridine (L) ligands has been an area of considerable interest in our laboratory[1–7] and elsewhere.[8–10] Quite a number of RuL complexes are now known, however there is no simple and direct synthetic route to them. The primary goal of the present paper is to report a single-pot high-yield synthesis of ruthenium bis and tris chelated compounds of L from $RuCl_3{\cdot}3H_2O$ with the use of $[AgL_2]ClO_4$.[11] The advantages of our new methods over the existing synthetic procedures are highlighted. We also report solid-state isomeric transformations of a bis ligated ruthenium(II) compound, $[RuCl_2L_2]$. The high stereospecificity of the isomerisation reactions makes the synthesis of a *cis* isomer more simple, fast and straightforward. The two ligands 2-(phenylazo)pyridine (pap,L^1) and 2-(*m*-tolylazo)pyridine (mtap,L^2) have been used.

Results and Discussion

(*a*) *Metal-exchange Reaction. Use of* $[AgL_2]^+$ *in Synthesis.*—Reactions (1)–(3) have been studied. Very recently we reported[11] the synthesis of four-co-ordinated silver(I) complexes of L which can be used as synthons for the synthesis of RuL complexes. The direct synthesis of bis and tris complexes from $RuCl_3$, as evidenced by the reactions (1)–(3), requires stepwise removal of Cl^- followed by co-ordination of L to the metal centre. Thus, it was anticipated that interaction of $RuCl_3$ and $[AgL_2]^+$ in appropriate proportion might lead directly to the desired compound. Accordingly, reactions (1)–(3) led smoothly to bis- and tris-chelated ruthenium complexes of L. The compound $[AgL_2]^+$ acts not only as a source of Ag^+ required for a facile halide-displacement reaction, but also supplies the required amount of L for formation of the complex of desired composition. It is believed that the reduction of the metal centre in each of reactions (1) and (2) is achieved[1] by the solvent. The tris chelates are isolated as their perchlorate salts. The dichloro bis chelates, which are sparingly soluble in methanol, precipitate from the reaction mixture. In all cases the compounds are isolated in high yields (*ca.* 70%). It may be noted that the excess of L [equations (2) and (3)] can be recovered from the reaction mixture (Experimental section).

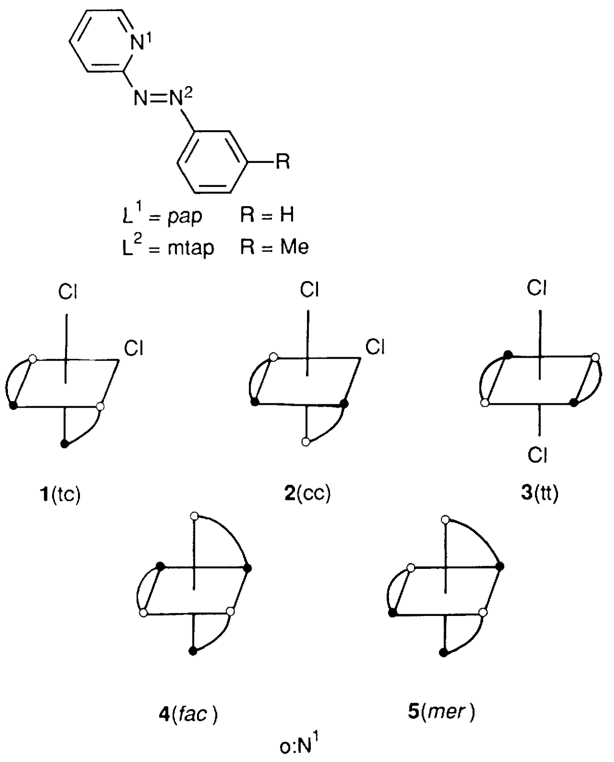
$$RuCl_3 + [AgL_2]^+ \xrightarrow{CH_3OH} [RuCl_2L_2] + AgCl \quad (1)$$

$$RuCl_3 + 3[AgL_2]^+ \xrightarrow{CH_3OH} [RuL_3]^{2+} + 3AgCl + 3L \quad (2)$$

$$[RuCl_2L_2] + 2[AgL_2]^+ \xrightarrow{CH_3OH} [RuL_3]^{2+} + 2AgCl + 3L \quad (3)$$

These new methods of preparation are straightforward and much more convenient than those reported previously. The existing methods for the synthesis of both $[RuL_3]^{2+}$ and $[RuCl_2L_2]$ involve[5] several steps which are not only time consuming but also require extra purification in every step to remove contaminates. On the other hand, the synthetic methods developed by us are single step, quite fast, produce compounds of desired composition in high yields and are experimentally facile. Moreover, the compositions of the products can be monitored just by varying the stoichiometric ratio of the reactants. In most cases recrystallisation, alone, produced isomerically pure compounds.

(*b*) *Separation and Identification of Isomers.*—While $[RuCl_2L_2]$ exists in three geometric forms,[1,8,10] two blue (**1**, **2**) and the third green (**3**), $[RuL_3]^{2+}$ exists[5] in either facial (**4**) or meridional geometry (**5**). Reaction (1) when carried out at *ca.* 40 °C for 15 min yielded 5–8% **1**, 5–10% **2** and 60–65% **3**. The isomers were purified and isolated either by solvent extraction or by chromatography on a silica gel column using a $CHCl_3$–CH_3CN mixture as eluent (Experimental section). The analytical, spectral and molar conductance data of the compounds are in accord with the literature.[1,5,8] The geometries of the products were identified by comparing their spectral data with those of authentic samples. The product obtained from reaction (2) yielded pure meridional isomer **5**, as evidenced by the ^1H NMR spectrum. The methyl signals of the L^2 complex were used to probe its stereochemistry. It shows three signals of equal intensity at δ 2.06, 2.20 and 2.27. Thus, all three ligands in $[RuL^2{}_3]^{2+}$ are non-equivalent which is expected[5,12] for a meridional structure. This observation is in contrast to our earlier experiment where it was reported[5] that for the meridional isomer two methyl signals of relative intensity 1:2 were observed. The geometry of the product of reaction (3) depends on that of the starting compound $[RuCl_2L_2]$: *trans,trans* (tt)-$[RuCl_2L_2]$ **3** is unreactive under our experimental conditions; the *trans,cis* (tc) isomer **1** yields pure meridional **5** whereas the cc isomer **2** yields **5** as a major product together with a small amount of the facial isomer.



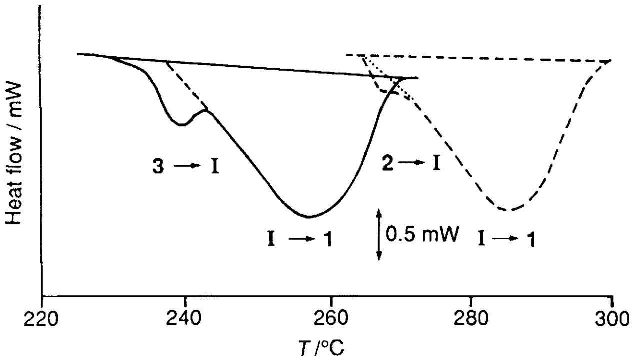


Fig. 1 DSC curves showing the transformations 3 ⟶ 1 (——) and 2 ⟶ 1 (– – –)

(*c*) *Solid-state Thermal Isomerisation*.—We have found that both the pure tt (**3**) and cc (**2**) isomers of [$RuCl_2L_2$] or an isomeric mixture of [$RuCl_2L_2$] produce tc-[$RuCl_2L_2$] on heating in the solid state. These transformations are quite fast and the yield is almost quantitative [*ca.* 90%, reaction (4)].

$$\text{tt/cc-[RuCl}_2\text{L}_2] \xrightarrow{\text{Heat}} \text{tc-[RuCl}_2\text{L}_2] \qquad (4)$$

Thermolysis of an isomeric mixture of [$RuCl_2L_2$] at *ca.* 270 °C leading to pure tc-[$RuCl_2L_2$] appears to be a useful way of accessing the compound in tc geometry. In order to gain some insight into the isomerisation of [$RuCl_2L_2$] species in the solid state, we investigated the solid-phase thermal reaction in the temperature range 30–300 °C by TG, DT and DSC experiments. The TG curves in both cases (**2**, **3**) remain flat up to 300 °C. The DT curve of **3** shows an exothermic peak at 255 °C whereas in case of **2** an exothermic transition was recorded at 285 °C. In both cases the spectral data for the compounds isolated after the transitions were identical to those for the corresponding tc isomer **1**. It may be noted that the DT curve of **1** is flat in the aforesaid temperature range, indicating that the isomer is stable up to 300 °C. The DSC experiments for isomers **3** (L = L^1) and **2** show (Fig. 1) that the tt isomer **3** undergoes an exothermic irreversible transition (227–269 °C, $\Delta H = -13.1$ kJ mol^{-1}), whereas for the cc isomer **2** the transition occurs from 265 to 299 °C ($\Delta H = -10.9$ kJ mol^{-1}) to form the tc isomer **1**. In each case there is a small peak at lower temperature indicating that the transitions (**2** or **3** ⟶ **1**) involve two steps and go through an intermediate **I** [equations (6) and (7)].

$$\mathbf{3} \longrightarrow \mathbf{I} \longrightarrow \mathbf{1},\ \Delta H = -13.1\ \text{kJ mol}^{-1} \qquad (6)$$

$$\mathbf{2} \longrightarrow \mathbf{I} \longrightarrow \mathbf{1},\ \Delta H = -10.9\ \text{kJ mol}^{-1} \qquad (7)$$

It is interesting that the area bounded by the curve for the second step of the transformation (*i.e.* **I** ⟶ **1**) of reaction (6) is almost equal to that of reaction (7). This implies that the heat liberated, once the intermediate **I** is formed, is the same for both reactions. This tempts us to predict that the isomerisation reactions go through a similar intermediate **I**. The temperature required for conversion **2** ⟶ **1** is higher than that for **3** ⟶ **1**. This indicates that the cc isomer **2** requires a higher activation energy to form the intermediate **I**. The very fact that the isomerisation processes are exothermic reveals that the tc isomer **1** is the most thermally stable.

The information obtained helped us to design a solid-state synthetic route to tc-[$RuCl_2L_2$] from [$RuCl_2(dmso)_4$] (dmso = dimethyl sulphoxide) and L. The reaction in neat L at 230 °C proceeds smoothly to produce tc-[$RuCl_2L_2$] [equation (8)] in

$$[\text{RuCl}_2(\text{dmso})_4] \xrightarrow[\textit{ca.}\ 230\ ^\circ\text{C}]{\text{neat L}} \text{tc-[RuCl}_2L_2] \qquad (8)$$

almost quantitative yield. It is very fast, being complete in less than 5 min.

Conclusion

It is demonstrated that the synthesis of both bis and tris chelated ruthenium complexes of L can easily be achieved directly from $RuCl_3 \cdot 3H_2O$ with the use of [AgL_2]ClO_4. The compositions of the products can be monitored just by varying the stoichiometric ratio of the reactants. The synthetic routes developed are experimentally facile and seem to be general for the synthesis of transition-metal complexes of polypyridyl and related ligand systems. The dichloride complexes **2** and **3** undergo solid-state thermal isomerisation to produce the thermally most stable isomer **1**. We note[13,14] that, to our knowledge, these are the first examples of solid-state geometrical thermal isomerisation reactions in ruthenium chemistry.

Experimental

Materials.—The salt [AgL_2]ClO_4 was synthesised as before.[11] **CAUTION**: Most perchlorate salts of the complexes are explosive. Adequate care should be taken while handling perchlorates.

The complex [$RuCl_2(dmso)_4$] was prepared by a published procedure,[15] $RuCl_3 \cdot 3H_2O$ was obtained from Arora Matthey, Calcutta. Spectrograde solvents were used for spectrochemical work. All other chemicals and solvents for preparative work were of reagent grade used without further purification.

Physical Measurements.—Spectroscopic data were obtained with the following instruments: electronic, Hitachi 330; IR (KBr disc, 4000–600 cm^{-1}), Perkin-Elmer IR-297; ^{1}H NMR [$(CD_3)_2SO$], Varian EM 390 spectrophotometer. Solution electrical conductivity was measured using a Elico CM 82T conductivity bridge with a solution concentration of *ca.* 10^{-3} mol dm^{-3}. Solid-state thermal investigations were carried out with a Perkin-Elmer DSC-7 differential scanning calorimeter and a Shimadzu DT-30 thermal analyser.

Syntheses.—(*i*) *Reaction of* $RuCl_3 \cdot 3H_2O$ *with* [AgL_2]ClO_4 *in* 1:1 *Molar Proportion*.—The reactions with [AgL_2]$^+$ [L = 2-

(phenylazo)pyridine (L^1) or 2-(*m*-tolylazo)pyridine (L^2)] were performed by using the general procedure described below.

The salt $RuCl_3{\cdot}3H_2O$ (1 mmol) was dissolved in methanol (15 cm^3) and to it a solution of $[AgL_2]ClO_4$ (1 mmol) in methanol (15 cm^3) was added. This mixture was warmed on a water bath (40 °C) for 15 min and then cooled. A green precipitate separated. It was filtered through a G-4 sintered glass funnel and washed three times with portions (10 cm^3) of methanol and dried in vacuum. It was then extracted with the minimum volume (50 cm^3) of dichlomethane to remove insoluble AgCl. On addition of hexane to the green solution, green flakes of tt-$[RuCl_2L_2]$ **3** were obtained. The complex was filtered off and dried *in vacuo* over P_4O_{10}.

The methanolic filtrate and washings obtained above were concentrated to *ca.* 15 cm^3 and on addition of an equal volume of water an isomeric mixture of $[RuCl_2L_2]$ separated which was collected by filtration. It was dried and subjected to chromatography on a silica gel column using different mixtures of dichloromethane–acetonitrile as eluent. The first green band was eluted with CH_3CN–CH_2Cl_2 (1:10). The other two bands, *viz.* blue and blue-violet, were eluted respectively with CH_3CN–CH_2Cl_2 (2:10 and 3:10). All the bands collected were crystallised by addition of hexane. The analytical and spectral data for the synthesised compounds correspond exactly[1,8] to those of authentic samples of $[RuCl_2L_2]$. Yields: green band, tt-$[RuCl_2(L^1)_2]$, 70%; blue band, tc-$[RuCl_2(L^1)_2]$, 10%; blue-violet band, cc-$[RuCl_2(L^1)_2]$, 8%. From a similar experiment starting from $[AgL_2{}^2]ClO_4$ and $RuCl_3$ the following complexes were obtained: tt-$[RuCl_2L^2{}_2]$, 70%; tc-$[RuCl_2L^2{}_2]$, 10%; cc-$[RuCl_2L^2{}_2]$, 8%.

(*ii*) *Reaction of* $RuCl_3{\cdot}3H_2O$ *with* $[AgL_2]ClO_4$ ($L = L^1$ *or* L^2) *in* 1:3 *Molar Proportion.*—The reactions were performed by using the general procedure described below.

A sample of $RuCl_3{\cdot}3H_2O$ (1 mmol) was dissolved in methanol (15 cm^3) and to it a solution of $[AgL_2]ClO_4$ (3 mmol) in methanol (15 cm^3) was added and the mixture was heated to reflux for 1 h. The mixture was cooled and filtered through a G-4 sintered glass funnel to remove insoluble AgCl. The filtrate was concentrated to *ca.* 10 cm^3 and an equal volume of diethyl ether was added. The brown precipitate of $[RuL_3][ClO_4]_2{\cdot}H_2O$ thus formed was collected by filtration. The colour of the filtrate was orange. The product on recrystallisation from water yielded a highly crystalline brown compound (yield 70%). Analytical spectral and molar conductance data for the synthesised complexes compare[5] very well with those of authentic samples of *mer*-$[RuL_3][ClO_4]_2{\cdot}H_2O$.

The orange filtrate obtained was evaporated to dryness and then extracted with hexane. The orange hexane solution on evaporation yielded free L. A similar experiment starting from $[AgL^2{}_2]ClO_4$ (3 mol) and $RuCl_3{\cdot}3H_2O$ (1 mol) yielded *mer*-$[RuL^2{}_3][ClO_4]_2{\cdot}H_2O$ in 70% yield.

(*iii*) *Reaction of* $[RuCl_2L^2{}_2]$ *with* $[AgL^2{}_2]ClO_4$ *in* 1:2 *Molar Proportion.*—To a suspension of tc-$[RuCl_2L^2{}_2]$ (0.566 g, 1 mmol) in methanol (15 cm^3) was added a solution of $[AgL^2{}_2]ClO_4$ (1.203 g, 2 mmol) in methanol (15 cm^3) and heated to reflux for 30 min. The procedure followed was then exactly that described in section (*ii*). Yield 85%. The reaction with cc-$[RuCl_2L^2{}_2]$ and $[AgL^2{}_2]ClO_4$ was performed similarly as described above. Yield 90%.

(*iv*) *Solid-state Thermal Isomerisation.*—tt-$[RuCl_2L^1{}_2] \longrightarrow$ tc-$[RuCl_2L^1{}_2]$.—A sample of tt-$[RuCl_2L^1{}_2]$ (0.538 g, 1 mmol) was placed in a round bottom flask (50 cm^{-3}) fitted with a condenser. It was then heated slowly in an oil-bath. The temperature was raised to 250 °C and maintained for 5 min. During heating the conversion of green flakes into dark shiny crystals was observed. The solid mass was extracted with the minimum volume (*ca.* 100 cm^3) of CH_2Cl_2. The volume was then reduced to 25 cm^3 and on addition of hexane dark shiny crystals of tc-$[RuCl_2L^1{}_2]$ separated which were collected by filtration and dried *in vacuo* over P_4O_{10}. Yield 90%. The conversion cc-$[RuCl_2L^1{}_2] \longrightarrow$ tc-$[RuCl_2L^1{}_2]$ was similarly performed. The temperature required for this transformation is 280 °C. Yield 90%.

(*v*) *Reaction of* $[RuCl_2(dmso)_4]$ *in Neat* L^1.—The complex $[RuCl_2(dmso)_4]$ (0.484 g, 1 mmol) and L^1 (0.366 g, 2 mmol) were thoroughly mixed in a round bottom flask (50 cm^3) fitted with a condenser and heated on an oil-bath at *ca.* 200 °C for 15 min. The dark mass was extracted with the minimum volume of CH_2Cl_2 (*ca.* 100 cm^3), the volume of the solution (deep blue) reduced to 25 cm^3 and hexane (50 cm^3) added. Dark shiny crystals of tc-$[RuCl_2L^1{}_2]$ separated, were collected by filtration and dried *in vacuo* over P_4O_{10}. Yield 90%.

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