Isolation, Characterization, and Kinetics of Formation of the *cis* and *trans* Isomers of Bis(acetonitrile)dichloroplatinum(II)

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The bis(acetonitrile)dichloroplatinum(II) obtained by the standard procedure has been shown to be a mixture of the *cis* and *trans* isomers the composition of which depends upon the experimental conditions used. The pure isomers have been characterized by i.r. and ^{1}H n.m.r. spectroscopy and the conditions for the preferential obtainment of each isomer have been explored. Kinetic measurements have shown that the formation of the *cis* isomer is kinetically favoured in the reaction of $[PtCl_3(NCMe)]^-$ with a second molecule of acetonitrile, indicating that the chlorine ligand exerts a *trans*-labilizing effect greater than that of acetonitrile.

The complex $[PtCl_2(NCMe)_2]$ was first prepared by Hoffmann and Bugge[1] in 1907 and postulated to have a *cis* configuration on the basis of chemical reactivity and i.r. data.[2,3] It is to be noted that the analogous complex of palladium, prepared by the same procedure, has instead a *trans* configuration.[4] The structure of single crystals of $[PtCl_2(NCMe)_2]$ was determined by different groups and always a *cis* configuration, with Pt–Cl and Pt–N bond lengths slightly shorter than normal, was found.[5]

In the present study we have carried out a detailed examination of the product obtained by the standard procedure[1] and found that it is a mixture of the *cis* and *trans* isomers, the composition of which strongly depends upon the experimental conditions used. This gives a clue to the unexpected *trans* configuration of several reaction products derived from this substrate.[6–8] We have also determined the experimental conditions for the obtainment of the pure isomers and carried out a kinetic study on the rate of formation of the two species.

Results and Discussion

Preparation of Complexes.—The Hoffmann reaction has been performed at 25 and 75 °C. When aqueous $K_2[PtCl_4]$ and MeCN (molar ratio 1:16) are allowed to react at 25 °C for 8d the yellow precipitate which separates is of the *cis* isomer containing a certain amount of the *trans* form (*ca.* 16%); the two species can easily be detected by t.l.c. on silica gel [eluant: dichloromethane–acetone (9:1, v/v)]. A quantitative separation of the two isomers can be accomplished by column chromatography on silica gel, the *trans* isomer being eluted first with dichloromethane–acetone (9:1, v/v), the *cis* isomer afterwards with pure acetone. Performing the same reaction at 75 °C for 3 h [time required for complete disappearance of the characteristic colour of tetrachloroplatinate(II) in aqueous solution], the composition of the precipitate is totally different, being now the *trans* isomer as the major component and the *cis* isomer less than 1%. The *trans* isomer can be obtained in a pure form by washing the raw material with acetonitrile which removes the more soluble *cis* isomer. The reaction performed at 75 °C also leads to the formation of a significant amount of the ionic complex $K[PtCl_3(NCMe)]$ which is soluble in the mother-liquor.[9] It can be isolated by evaporation of the solvent and extraction of the solid residue with cold methanol or acetone.

On varying the solvent composition (acetonitrile–water) from 1:20 to 1:4, v/v the isomeric ratio does not change significantly but the rate of formation of $[PtCl_2(NCMe)_2]$ decreases as the concentration of acetonitrile becomes smaller. If a suspension of the *cis* isomer in aqueous acetonitrile (12:1, v/v) is kept at 75 °C for a few hours a nearly complete transformation into the *trans* form is observed. These results can be interpreted in the following way: at low temperature the *cis* isomer is formed in preference because it is kinetically favoured; on increasing the temperature an isomerization of the complex can take place and the *trans* isomer, being less soluble than the *cis* form in the given solvent, precipitate preferentially.

Characterization of the Isomers.—The two isomers have different solubility and chromatographic behaviour {the *trans* isomer is less soluble in polar solvents such as acetonitrile and acetone and it is also more mobile under chromatographic conditions as already observed for the corresponding isomers of $[PtCl_2(NCPh)_2]$}.[10]

The i.r. spectra of the *cis* and *trans* isomers of $[PtCl_2(NCMe)_2]$ as well as that of $K[PtCl_3(NCMe)]$ are shown in Figure 1. It is worth noting that the band multiplicity does not change greatly for the different species although the relative intensities do change. This could explain why the presence of different isomers has not been early recognized. (The situation was slightly better in the case of the benzonitrile analogues where significant differences between the two isomers were observable in the 800—650 cm^{-1} region where the out-of-plane CH deformation vibrations of the phenyl groups occur.[4,10]) In the platinum–chlorine stretching region the *cis* isomer exhibits two bands at 356 and 350 cm^{-1}, the *trans* isomer only one band at 345 cm^{-1}; this could be diagnostic for the identification of the two isomers however it is worth remembering that the corresponding complex with benzonitrile showed, in the same region, two and three bands for the *cis* and *trans* isomer, respectively.[10]

Only one resonance is observed in the ^{1}H n.m.r. spectra of either isomer. The values [chemical shift (^{195}Pt coupling constant)] in deuterioacetone were δ 2.750(15), 2.655(13), 2.500(15 Hz), and 2.035 for *trans*-$[PtCl_2(NCMe)_2]$, *cis*-$[PtCl_2(NCMe)_2]$, $[PtCl_3(NCMe)]^-$, and NCMe respectively. The differences in chemical shifts and coupling constants between different isomers are not great but still significant. The downfield shift, with respect to the free ligand, is greater for the neutral bis adducts than for the negatively charged mono adduct, moreover the downfield shift and ^{195}Pt coupling constant are greater for the *trans* than for the *cis* isomer, in accord with a smaller *trans* influence of acetonitrile with respect to chlorine (see further discussion below).

Kinetic Data.—Although there were strong indications (see preparation of complexes) that the formation of the *cis* isomer was favoured in the kinetics of addition of a second acetonitrile

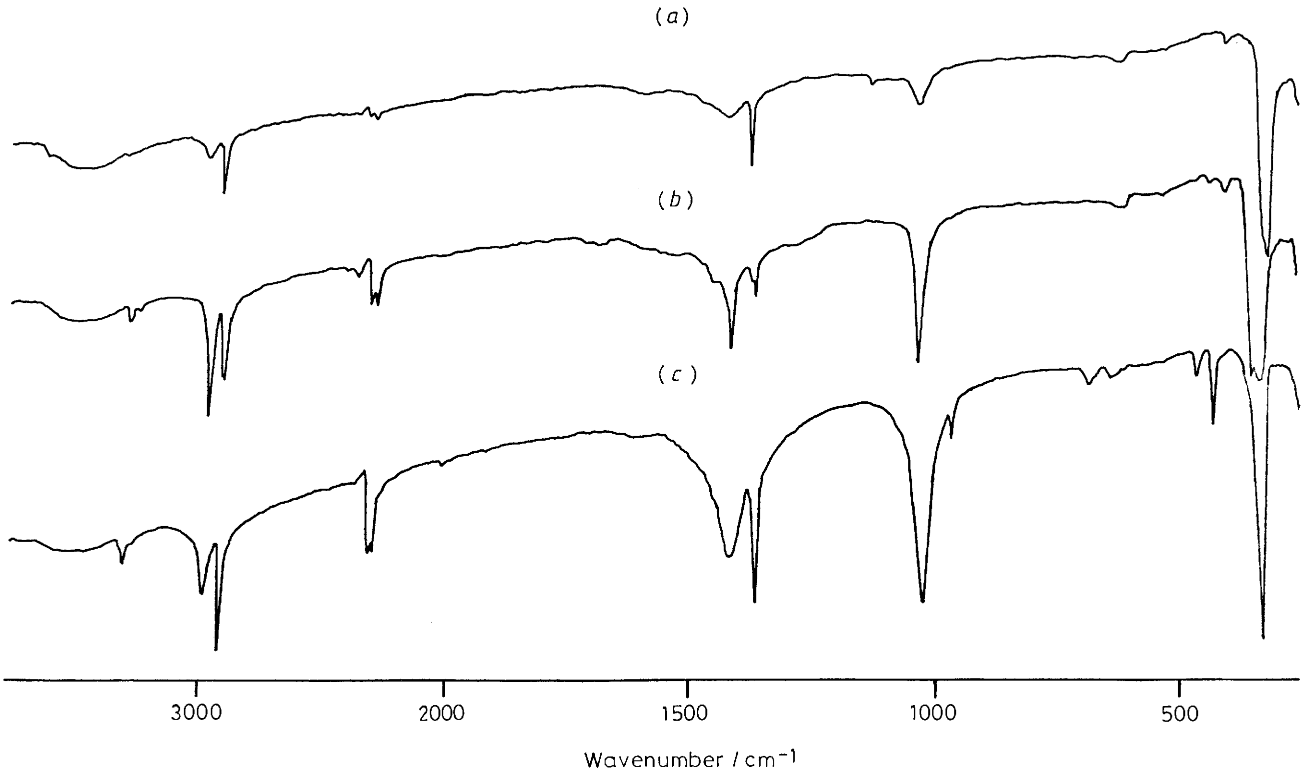


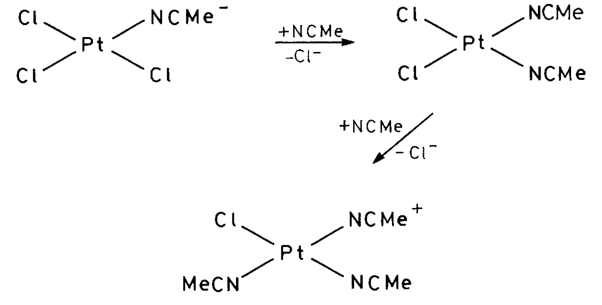
Figure 1. I.r. spectra of (*a*) K[PtCl$_3$(NCMe)], (*b*) *cis*-[PtCl$_2$(NCMe)$_2$], and (*c*) *trans*-[PtCl$_2$(NCMe)$_2$]

to [PtCl$_3$(NCMe)]$^-$ and that the *trans* isomer was formed by isomerization of the *cis* form, a conclusive answer to this question could come from a kinetic study.

We chose as solvent water–acetonitrile (2:1, v/v) since it dissolves a sufficient amount of all different species and contains enough acetonitrile to ensure a relatively rapid rate of formation of the bis adduct starting from the mono adduct; moreover this solvent composition is not very much different from that used under preparative conditions. The bis(acetonitrile) derivatives, however, are not stable in this solvent but undergo a further substitution of the chlorine ligands by solvent molecules (Figure 2). In the case of the *cis* isomer the spectral changes show a clear isosbestic point at 308 nm and the $k_{obs.}$ for this transformation is $(1.4 \pm 0.1) \times 10^{-5}$ s^{-1} [35 °C; water–acetonitrile (2:1, v/v)]. Under strictly analogous conditions the *trans* isomer undergoes a more complex spectral change with the appearance of a delayed isosbestic point at 308 nm; the changes of absorbance at 308 nm obey first-order kinetics and give a $k_{obs.}$ value of $(2.2 \pm 0.2) \times 10^{-4}$ s^{-1}. Beyond any reasonable doubt the faster process corresponds to the solvolysis of the *trans* isomer while the slower transformation, with the isosbestic point at 308 nm and an overall spectral change similar to that observed in the final stage of the solvolysis of the *cis* isomer, should correspond to the solvolysis of a small amount of the *cis* isomer formed in the initial process. (Another possible explanation is that the newly formed solvato species undergoes a further transformation which is more rapid, compared to the rate of solvolysis, in the case of the *cis* isomer, but slower in the case of the *trans* species.)

The observation that the rate of solvolysis is faster (by a factor of sixteen) in the *trans* complex (leaving chloride *trans* to a chloride ligand) than it is in the *cis* isomer (leaving chloride *trans* to the acetonitrile) is a clear indication that the chlorine ligand exerts a much greater *trans*-labilizing effect than the acetonitrile.

The kinetics of transformation of K[PtCl$_3$(NCMe)] was also studied under similar conditions. Once again the spectral changes were rather complex with the appearance of a delayed isosbestic point at 308 nm (Figure 2). At this wavelength the changes of absorbance followed first-order kinetics with $k_{obs.}$ $(6.4 \pm 0.5) \times 10^{-5}$ s^{-1}. This rate constant is greater (by a factor of 4.5) than the rate of solvolysis of the *cis* isomer of [PtCl$_2$(NCMe)$_2$] but smaller (by a factor of 3.5) than the rate of solvolysis of the *trans* isomer. Therefore a two-step reaction is only in accord with the formation of first *cis*-[PtCl$_2$(NCMe)$_2$] followed by solvolysis of this species (Scheme). In the case in which the *trans* isomer was the first product to be formed, only one process (its formation but not solvolysis) would have been observed.



Scheme.

Conclusions

The isolation of the *cis* and *trans* isomers of [PtCl$_2$(NCMe)$_2$] has been shown to depend upon kinetic and thermodynamic factors. The *cis* isomer is kinetically favoured in the reaction of [PtCl$_3$(NCMe)]$^-$ with acetonitrile and can be obtained to a greater extent by performing the reaction at low temperature (25 °C). The transformation of the *cis* into the *trans* complex can be accomplished by warming (75 °C) for a few hours a sus-

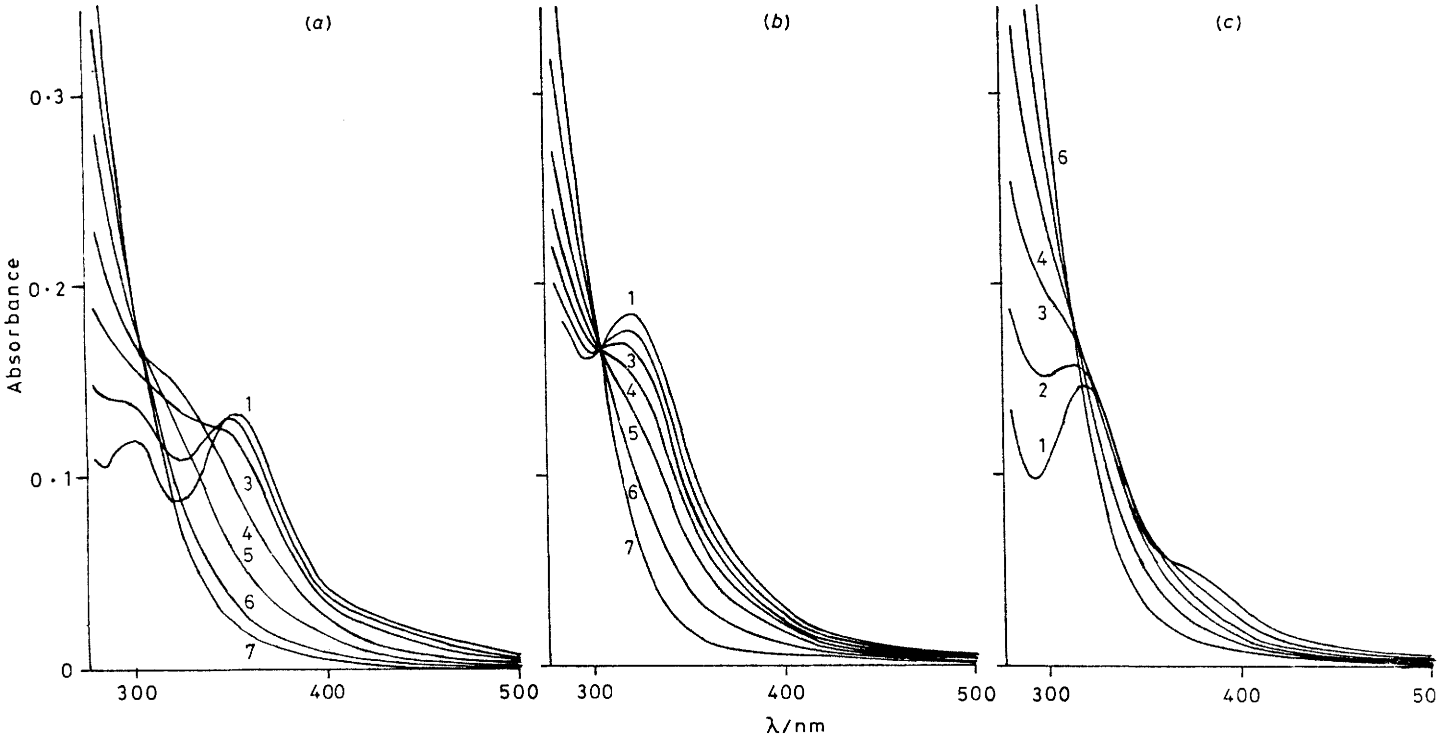


Figure 2. Spectral changes with time in a solution of (*a*) K[PtCl$_3$(NCMe)], (*b*) *cis*-[PtCl$_2$(NCMe)$_2$], and (*c*) *trans*-[PtCl$_2$(NCMe)$_2$]. Solvent: water–acetonitrile (2:1, v/v). Temperature, 35 °C. Time (min): (*a*) 0, 75, 250, 470, 1 300, 2 800, and 5 000 for 1—7; (*b*) 0, 148, 288, 485, 788, 1 538, and 5 000 for 1—7; (*c*) 0, 30, 90, 210, 450, and 1 500 for 1—6

pension of the *cis* form in water containing 10% acetonitrile; the high temperature favours the isomerization reaction and the *trans* species, which is less soluble than the *cis* isomer in polar solvents, precipitates preferentially.

It is likely that also in the reaction of tetrachloropalladate(II) with acetonitrile, performed under the Hoffmann conditions, the *cis* isomer of [PdCl$_2$(NCMe)$_2$] is the first product but, owing to the greater lability of the palladium complexes as compared to the platinum analogues,[11] the *cis* isomer isomerizes to the less-soluble *trans* species even at room temperature so that the latter becomes the only isolable species.[4]

Experimental

Starting Materials.—Commercial reagent grade chemicals were used without further purification. The complexes *cis*- and *trans*-[PtCl$_2$(NCMe)$_2$] were prepared by the standard procedure of Hoffmann and Bugge[1] from potassium tetrachloroplatinate(II) and acetonitrile. The reaction was performed at 25 and 75 °C.

At 25 °C a solution of K$_2$[PtCl$_4$] (2.0 g, 4.8 mmol) and acetonitrile (3.0 g, 73 mmol) in water (40 cm^3) was left stirring for 1 week. The yellow precipitate which developed was collected, washed with water, and dried in air. This compound, analyzed by h.p.l.c., was a mixture of the *cis* and *trans* isomers in *ca.* 5:1 ratio. A complete separation of the *cis* and *trans* isomers can be accomplished by chromatography on an open column of silica gel using dichloromethane–acetone as eluant. At 75 °C the reaction of K$_2$[PtCl$_4$] and acetonitrile in water is complete in 3 h. The yellow precipitate, washed with water and dried, was almost exclusively the *trans* isomer containing only a trace amount of the *cis* form (less than 1%). Pure *trans* isomer can be obtained by carefully washing the crude reaction product with acetonitrile which dissolves the more-soluble *cis* form (yield *ca.* 50%). The reaction performed at 75 °C also leads to the formation of a certain amount of K[PtCl$_3$(NCMe)] which can be recovered from the aqueous solution by evaporation of the solvent and extraction of the solid residue with methanol. Yield *ca.* 30%.

Kinetics.—Rate data were obtained spectrophotometrically by measuring changes of absorbance with time. The complex was dissolved directly in a thermostatted water–acetonitrile (2:1, v/v) solution and the change of absorbance monitored as a function of time. First-order rate constants were calculated from plots of $\ln(A_\infty - A_t)$ against time, where A_t and A_∞ are absorbances at time t and after at least six half-lives, respectively. These plots were linear for at least six half-lives; the gradients were calculated from least-squares fits and the quoted uncertainties are 95% confidence limits.

Physical Measurements.—I.r. spectra in the range 4 000—250 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 683 spectrophotometer, ^{1}H n.m.r. spectra with a Varian XL 200 spectrometer. H.p.l.c. analyses were performed on a Waters chromatograph equipped with an U6-K universal injector, a model 501 solvent-delivery system, a differential u.v. detector (254 nm), and a LiChrosorb CN column (7 µm, 25 cm × 4.2 mm I.D.). The eluant was dichloromethane–n-hexane (70:30, v/v). U.v.–visible spectra were recorded on a Varian 2200 double-beam spectrophotometer.

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