

A PAPER CHROMATOGRAPHIC STUDY OF SOME PLATINUM (II) COMPOUNDS

II. THE SEPARATION OF *cis*- AND *trans*-DIHALOGENODIAMMINEPLATINUM (II) COMPLEXES

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INTRODUCTION

In a preceding paper¹ the separation of the *cis*- and *trans*-[Pt(NH₃)₂Cl₂]⁰ complexes from each other and from other platinum (II) complexes was described using aqueous solvents as eluents on cellulose filter paper. This kind of adsorption cellulose chromatography appeared of interest since the adsorption mechanism of neutral complexes had not been previously investigated². In addition preparative work (by F.B. and K.H.S.) also required a method for establishing the purity of the dibromo-, diiodo-, chloriodo- and chlorobromo-diammineplatinum(II) complexes. Thus this paper reports the general study made on these halogeno complexes. The choice of methods is rather limited. Owing to the non-ionic character of all the compounds, ion exchange and paper electrophoretic methods are clearly unsuitable. During preliminary experiments it was also found that development for more than 1-2 h with partition solvents (such as butanol-water, butanol-1 *N* HCl etc.) produced long comets indicating transformations during the development. The presence of mineral acids even as dilute as 0.1 *N* led to substitution reactions at room temperature during a short development. Good separations were finally obtained by using neutral solvents under such conditions as to minimize hydrolysis during development.

TECHNIQUE

Ascending development in tightly closing jars (26 cm × 12 cm) was used throughout with Whatman No. 3 MM paper. Samples had to be dissolved in water only minutes before being placed on the paper to avoid hydrolysis. All spots were shown up on the developed chromatogram by holding the paper over iodine vapours which, depending on the compound, yielded yellow, brown or violet spots on a paler background. All *R_F* values given here are strictly relative. Considerable variations were observed from day to day and from one batch of paper to another. Thus the absolute *R_F* values for example in Tables I-IV are only indicative: however, the *R_F* differences are always readily reproducible. For identification purposes reference substances must be run on the same sheet of paper with the samples to be tested.

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EXPERIMENTAL

(i) Studies on the adsorption of cis- and trans-[Pt(NH₃)₂Cl₂]⁰

The R_F values of *cis*- and *trans*-[Pt(NH₃)₂Cl₂]⁰ in HCl, LiCl, NaCl and KCl of varying concentration are shown in Fig. 1. Unlike with chlorauric acid and other chloro-acids³ there is no notable salting-out effect with these two complexes. However, it is interesting to note that the R_F values of the *cis*- and the *trans*-forms approach each other in higher concentrations of HCl. The adsorption seems to be related to the polarity

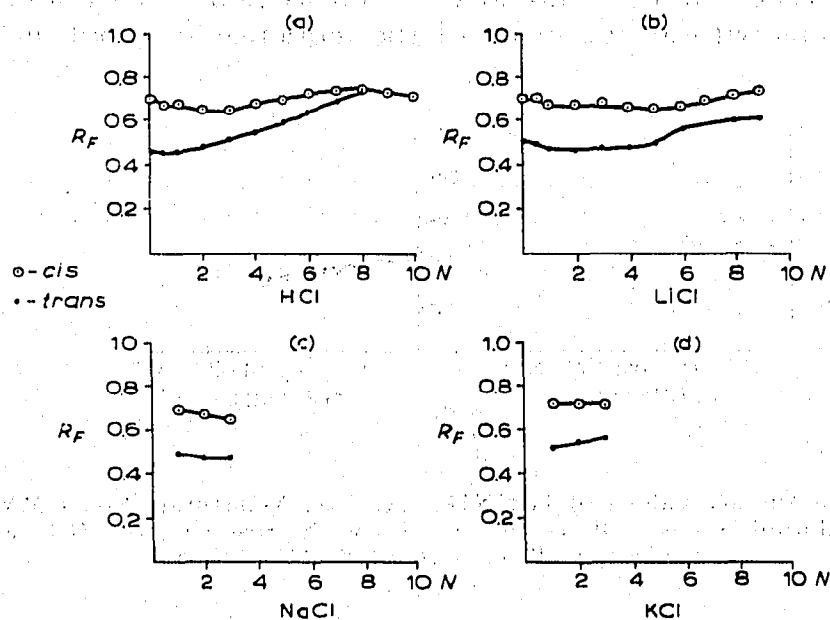


Fig. 1. The variation of the R_F values of *cis*- and *trans*-[Pt(NH₃)₂Cl₂]⁰ on Whatman No. 3 MM paper at 20°. Eluent: (a) aqueous HCl, 0.1–10 N; (b) aqueous LiCl, 0.1–9 N; (c) aqueous NaCl, 1–3 N; (d) aqueous KCl, 1–3 N.

of the complexes and their environment. Thus whenever the ionic cloud around both complexes is very large the differences in hydration (and adsorption) disappear. This agrees with the results in Fig. 2 which show the changes in R_F values of the two isomers with increasing concentrations of ethanol in 0.5 N HCl. Again the separability decreases with a decrease in the polarity of the solvent system.

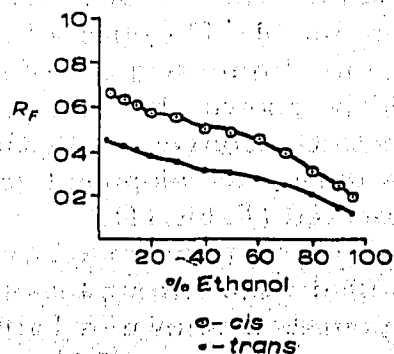


Fig. 2. The variation of the R_F values of *cis*- and *trans*-[Pt(NH₃)₂Cl₂]⁰ on Whatman No. 3 MM paper at 20° with alcoholic 0.5 N HCl.

(ii) Separations of the dichloro- dibromo- and diiodo-diammineplatinum(II) complexes

The first attempts were to use butanol-water as partition solvent for these compounds. Long trails were formed which indicated that under the dynamic conditions of development, the hydrolysis reactions were too fast to yield separations. In order to repress the extent of hydrolysis, it was decided to acidify (0.1 N HCl) the aqueous and ethanolic solvents. At room temperature ($18^\circ \pm 1^\circ$) the R_F values shown in Fig. 3a and 3b were obtained, thus it was possible to separate the *cis*-compounds from each other and from the *trans*-compounds, but not the *trans*-compounds from each other. The largest R_F differences were found to be in the region of very low or very high ethanol concentrations with an inversion of the sequence at about 40% ethanol.

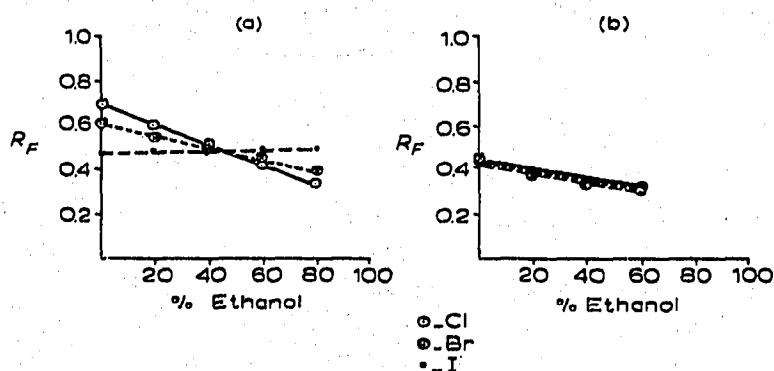


Fig. 3. The variation of the R_F values of $[\text{Pt}(\text{NH}_3)_2\text{X}_2]^0$ on Whatman No. 3 MM paper at 18° using mixtures of ethanol-water (all being 0.1 N with respect to HCl) as solvent. (a) *cis*- $[\text{Pt}(\text{NH}_3)_2\text{X}_2]^0$; (b) *trans*- $[\text{Pt}(\text{NH}_3)_2\text{X}_2]^0$.

It would appear that the adsorption differences are due to the hydration differences in aqueous solvents, the *cis*-diiodo being least hydrated and hence most adsorbed and the *cis*-dichloro being most hydrated and thus least adsorbed. This would be in accord with the greater electronegativity of chlorine *versus* iodine so that the dichloro system is expected to have the higher dipole moment and thus be more solvated. The *trans*-compounds having no dipole moment are not differentiated in aqueous solvents.

An attempt was made to apply these mixtures of ethanol-water (containing 0.1 N HCl) to the identification of the *cis*-chlorobromodiammineplatinum(II). However, it was noted that with a small increase in the room temperature (from 18° to 21°) the R_F values were no longer reproducible. The effect of temperature on the R_F values is shown in Table I. By carrying out chromatograms of solutions which were allowed to stand (in 0.1 N HCl) it could be shown that the change of R_F values was not due to temperature changes but to the conversion of the bromo complexes into the corresponding chloro complexes during development (see Table II). In 0.1 N HBr the reverse reaction could be observed (Table III).

Both hydrolysis and replacement reactions could be avoided by chromatographing in a refrigerator ($+5^\circ$) with distilled water. Round spots and good separations were obtained with all of the *cis*-compounds as shown in Table IV.

After obtaining these results, a search was made for solvents capable of separating the *trans*-compounds. This search was limited to fast flowing solvents without the

TABLE I

R_F VALUES OF *cis*-DIHALODIAMMINEPLATINUM (II) COMPLEXES AT VARIOUS TEMPERATURES
(Solvent: aqueous 0.1 N HCl; paper: Whatman No. 3 MM)

Complex	R_F		
	5°	18°	21°
Pt(NH ₃) ₂ Cl ₂	0.63	0.70	0.70
Pt(NH ₃) ₂ ClBr	0.60	—	0.68
Pt(NH ₃) ₂ Br ₂	0.54	0.62	0.66

TABLE II

EFFECT OF AGEING ON SOLUTIONS OF *cis*-DIHALODIAMMINEPLATINUM (II) IN 0.1 N HCl
(Paper: Whatman No. 3 MM; temperature for ageing and development: 18°)

Complex	R_F after ageing for:		
	0 h	7 h	24 h
Pt(NH ₃) ₂ Cl ₂	0.71	0.70	0.71
Pt(NH ₃) ₂ ClBr	0.68	0.69	0.71
Pt(NH ₃) ₂ Br ₂	0.64	0.67	0.68

TABLE III

EFFECT OF AGEING ON SOLUTIONS OF *cis*-DIHALODIAMMINEPLATINUM (II) IN 0.1 N HBr
(Paper: Whatman No. 3 MM; temperature for ageing and development: 18°)

Complex	R_F after ageing for:		
	0 h	12 h	24 h
Pt(NH ₃) ₂ Cl ₂	0.69	0.67	0.66
Pt(NH ₃) ₂ ClBr	0.66	0.66	0.66
Pt(NH ₃) ₂ Br ₂	0.60	0.62	0.64

TABLE IV

R_F VALUES OF *cis*-DIHALODIAMMINEPLATINUM (II) COMPLEXES
(Solvent: water; paper: Whatman No. 3 MM; temperature: 5°)

Complex	R_F
Pt(NH ₃) ₂ Cl ₂	0.65, 0.65, 0.65
Pt(NH ₃) ₂ ClBr	0.58, 0.58, 0.58
Pt(NH ₃) ₂ Br ₂	0.52, 0.53, 0.53
Pt(NH ₃) ₂ ClI	0.56
Pt(NH ₃) ₂ I ₂	0.44, 0.44, 0.43

addition of mineral acids. Neither pure methanol nor ethanol yielded good separations; however mixtures of acetone and water at 18° gave excellent separations of both the *cis*- and the *trans*-compounds.

The R_F values are shown in Fig. 4a and 4b.

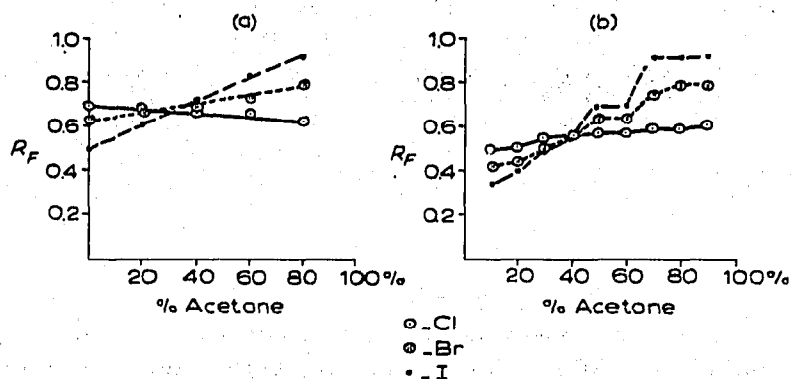


Fig. 4. (a) R_F values of *cis*-[Pt(NH₃)₂X₂]⁰ with acetone-water mixtures. Temperature: 20°; paper: Whatman No. 3 MM. (b) R_F values of *trans*-[Pt(NH₃)₂X₂]⁰ with acetone-water mixtures. Temperature: 20°; paper: Whatman No. 3 MM.

RESULTS

The *cis*- and *trans*-dibromo and diiodo complexes were all prepared by reacting the dichloro complex with two equivalents of AgNO₃, filtering off the precipitated AgCl and then adding two equivalents of either NaBr or KI. This resulted in the separation from solution of the desired compounds. Paper chromatography showed all these reactions to yield only a single spot corresponding to the dihalogeno complex of the

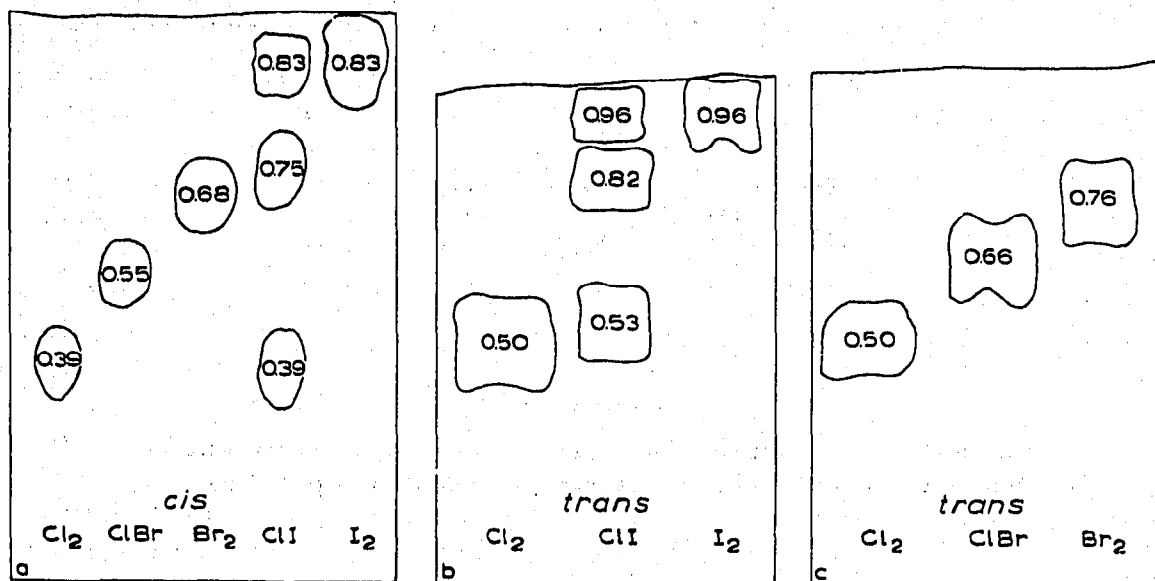


Fig. 5. Some typical chromatograms obtained with acetone-water (9:1) at 20° on Whatman No. 3 MM paper. Bottom line: line of application; top line: liquid front. (a) Samples of *cis*-[Pt(NH₃)₂X₂]⁰ run side by side on the same sheet. Note that *cis*-ClI is impure containing also *cis*-Cl₂ and I₂ complexes. (b) Samples of *trans*-[Pt(NH₃)₂X₂]⁰ run side by side on the same sheet. Note that *trans*-ClI contains also *trans*-Cl₂ and I₂ complexes. (c) Samples of *trans*-[Pt(NH₃)₂X₂]⁰ run side by side on the same sheet.

same geometric structure. It may thus be concluded that chromatographically pure compounds are formed by this reaction.

The mixed dihalogeno complexes were prepared by reaction of the required dichloro complex with one equivalent of AgNO_3 after which the precipitate of AgCl was removed on a filter and one equivalent of either NaBr or KI was added. The chlorobromo compounds so prepared were also found to be pure within the limits of detectability on a paper chromatogram. On the other hand the presumed chloriodo complexes yielded usually three spots: the dichloro, the chloriodo and the diiodo complexes (Fig. 5). The reaction of *trans*-dichloro with equivalent amounts of *trans*-diiodo in boiling water was also tried and yielded only a weak spot of the chloriodo complex in presence of preponderant quantities of the dichloro and the diiodo complexes.

The details of these syntheses as well as further preparative work will be described elsewhere.

SUMMARY

The separation of *cis*- and *trans*-dihalogenodiammineplatinum (II) complexes was effected by paper chromatography using neutral fast flowing solvents such as water at 5° or acetone-water (9:1). Practically all mixtures of *cis*- and *trans*- as well as of dichloro-, dibromo-, diiodo as well as chloriodo- and chlorobromo-complexes could be separated.

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