

CHROM. 17 607

## Note

### Effect of the geometric configuration of square-planar complexes on their $R_F$ values obtained by thin-layer chromatography on silica gel

GORDANA VUČKOVIĆ, T. J. JANJIĆ, Ž. Lj. TEŠIĆ and M. B. ČELAP\*

*Institute of Chemistry, Faculty of Science, University of Beograd, P.O. Box 550, 11001 Beograd (Yugoslavia)*

(Received January 30th, 1985)

In an earlier paper<sup>1</sup> we established that in thin-layer chromatographic separations of octahedral complexes on silica gel the *trans* isomers exhibit higher  $R_F$  values than the corresponding *cis* isomers, provided that single-component solvent systems are used. When multi-component solvent systems are used, this regularity was not observed.

Continuing these investigations, in this work we investigated whether the above regularity is valid for chromatographic separations of square-planar complexes.

#### EXPERIMENTAL

All the investigated complexes were synthesized according to the procedures reported in the literature (Table IV). The complexes were chromatographed by ascending thin-layer chromatography on silica gel DG (Riedel, Hannover, F.R.G.) and silica gel H, Type 60 (Merck, Darmstadt, F.R.G.). A suspension of 30 g of silica gel in 70 cm<sup>3</sup> of water was applied on five glass plates (19.5 × 13 × 0.5 cm). The layer thickness was about 300 μm. After being air-dried for 15 min, the plates were activated by heating them in a drying cabinet at 105–110°C for 1 h, and then they were kept in a desiccator over anhydrous calcium chloride. Solutions of complexes (Tables III and IV, complexes 1–6 in acetone, 7–10 in methanol, 11–16, 19 and 20 in chloroform and 17, 18, 21 and 22 in distilled water) were spotted as small drops. Development was carried out in glass vessels (13.5 × 19.5 × 23.5 cm), each solvent system being placed in the vessel 1 h before the chromatographic procedure, in order to saturate it with the solvent vapour. The compositions of the solvent systems used are given in Tables I and II. The spots were detected by means of iodine vapour. The reproducibility of the  $R_F$  values was ±0.03. All the investigations were performed at 20 ± 2°C.

#### RESULTS

As indicated in Tables III and IV, eleven pairs of geometrical isomers of Pt(II) and Pd(II) complexes were chromatographed on silica gel thin layers by use of 28 solvent systems. The complexes were of the neutral or cationic type, containing com-

TABLE I  
SINGLE-COMPONENT SOLVENT SYSTEMS USED

No.	Component	Time of development (min)
1	N,N-Dimethylformamide	25
2	Ethanol	40
3	Methanol	15
4	Methyl propyl ketone	15
5	Acetone	12
6	Ethyl methyl ketone	12
7	Ethylene glycol monomethyl ether	55
8	Distilled water	15
9	<i>n</i> -Butyl acetate	60
10	Ethylene glycol	120
11	Chloroform	15
12	Ethyl acetate	55
13	Formic acid	10
14	Acetylacetone	20

TABLE II  
MULTI-COMPONENT SOLVENT SYSTEMS USED

No.	Composition	Proportions (v/v)	Time of development (min)
15	Ethyl acetate-ethanol-water	50:30:20	40
16	Acetic acid-water	80:20	50
17	Acetic acid-water	50:50	40
18	Methanol-ethanol	50:50	30
19	Methanol-water	95:5	15
20	Methanol-formamide	60:40	25
21	Methanol-water-conc. nitric acid	75:20:5	30
22	<i>n</i> -Butanol-ethanol-water	70:20:10	40
23	Chloroform-benzene	95:5	12
24	Dioxan-water	90:10	30
25	Dioxan-water-potassium iodide	85:15:1 g per 100 ml	30
26	Ethyl acetate-ethanol	20:80	20
27	N,N-Dimethylformamide-water	95:5	25
28	Ethylene glycol monomethyl ether-water	90:10	45

binations of the following ligands: chloride, bromide, iodide, thiocyanate, ammonia, pyridine, quinoline, hydroxylamine and triphenylphosphine.

In addition, from Table III it can be seen that in all the 45 instances investigated the *trans* isomers exhibit higher  $R_F$  values than the corresponding *cis* isomers when single-component solvent systems are used. With multi-component solvent systems (Table IV), in 31% of cases the reverse order of the  $R_F$  values of the isomers is observed.

TABLE III  
EFFECT OF THE GEOMETRICAL CONFIGURATION OF SQUARE-PLANAR Pd(II) AND Pt(II) COMPLEXES ON THEIR  $R_F$  VALUES OBTAINED WITH SINGLE-COMPONENT SOLVENT SYSTEMS

No.	Isomer	Complex*	Ref.	$R_F \times 100^{**}$		1		2		3, H, 4, H, 5, H, 6, G, 7		8, G, 9, G, 10, G, 11, G, 12		13, H, 14, H		
				G***	H***	G	H	G	H	G	H	G	H	G	H	
1	cis-	$[\text{PtCl}_2(\text{NH}_3)_2]$	2	89	81	-	47	71	-	-	-	-	-	-	-	-
2	trans-		2	95	93	-	89	92	-	-	-	-	-	-	-	-
3	cis-	$[\text{PtBr}_2(\text{NH}_3)_2]$	3	-	-	60	47	82	30	-	-	-	-	-	-	-
4	trans-		3	-	-	96	91	93	96	-	-	-	-	-	-	-
5	cis-	$[\text{PtI}_2(\text{NH}_3)_2]$	3	-	-	-	-	-	65	80	87	-	-	-	-	-
6	trans-		3	-	-	-	-	-	97	89	94	-	-	-	-	-
7	cis-	$[\text{Pt}(\text{SCN})_2(\text{NH}_3)_2]$	4	85	-	89	86	75	71	95	91	-	-	-	-	-
8	trans-		4	89	-	99	94	91	83	91	98	95	-	-	-	-
9	cis-	$[\text{Pt}(\text{SCN})_2\text{py}_2]$	4	-	-	-	-	52	-	92	-	-	-	-	-	85
10	trans-		4	-	-	-	-	81	-	96	-	-	-	-	-	88
11	cis-	$[\text{PdCl}_2\text{py}_2]$	5	91	-	-	-	-	86	-	-	19	-	16	-	-
12	trans-		5	96	-	-	-	-	90	-	-	24	-	21	-	-
13	cis-	$[\text{PtCl}_2\text{qu}_2]$	6	-	-	-	79	-	85	-	-	-	8	-	75	12
14	trans-		6	-	-	-	91	-	88	-	-	-	24	-	81	22
15	cis-	$[\text{PtCl}_2\text{py}_2]$	7	-	87	-	-	-	-	71	-	-	7	8	13	69
16	trans-		7	-	91	-	-	-	-	88	-	-	31	24	72	79
17	cis-	$[\text{Pt}(\text{NH}_3)_2\text{hx}_2]^{2+}$	8	-	-	-	-	-	-	-	-	64	-	51	-	-
18	trans-		8	-	-	-	-	-	-	-	-	70	-	58	-	-
19	cis-	$[\text{Pt}(\text{P}\phi_3)_2\text{Cl}_2]$	9	-	79	-	-	-	93	-	-	-	21	-	82	76
20	trans-		10	-	92	-	-	-	97	-	-	-	25	-	91	93

\* py = Pyridine; qu = quinoline; hx = hydroxylamine;  $\text{P}\phi_3$  = triphenylphosphine.

\*\* The compositions of solvent systems 1-14 are given in Table I.

\*\*\* G = Silica gel; H = silica gel H.

TABLE IV  
EFFECT OF THE GEOMETRICAL CONFIGURATION OF SQUARE-PLANAR Pt(II) AND Pd(II) COMPLEXES ON THEIR  $R_f$  VALUES OBTAINED WITH MULTI-COMPONENT SOLVENT SYSTEMS

No.	Isomer	Complex*	Ref. $R_f \times 100^{**}$	15, G*** 16, H*** 17																		
				18, H	19, H	20, H	21, H	22, G	23, G	24, H	25, H	26, H	27, H	28, H								
				G		H																
1	cis-	[PtCl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	2	-	-	-	-	60	-	95	52	-	-	-	-	-	-	-	-	-		
2	trans-	[PtCl <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	2	-	-	-	-	63	-	89	84	-	-	-	-	-	-	-	-	-		
3	cis-	[PtBr <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3	87	-	-	-	68	-	90	65	-	-	-	-	-	-	-	-	87		
4	trans-	[PtBr <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3	95	-	-	-	85	-	93	92	-	-	-	-	-	-	-	-	97		
5	cis-	[PtI <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3	91	-	-	-	90	-	-	87	-	-	87	-	-	-	-	-	-		
6	trans-	[PtI <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	3	95	-	-	-	93	-	-	91	-	-	98	-	-	-	-	-	-		
7	cis-	[Pt(SCN) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	4	92	-	-	-	77	80	-	95	91	-	-	-	-	-	-	-	-		
8	trans-	[Pt(SCN) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	4	96	-	-	-	93	85	-	98	83	-	-	-	-	-	-	-	-		
9	cis-	[Pt(SCN) <sub>2</sub> py <sub>2</sub> ]	4	-	-	-	-	81	79	-	-	91	-	-	-	76	-	-	-	-		
10	trans-	[Pt(SCN) <sub>2</sub> py <sub>2</sub> ]	4	-	-	-	-	84	71	-	-	82	-	-	68	-	-	-	-	-		
11	cis-	[PdCl <sub>2</sub> py <sub>2</sub> ]	5	-	89	-	-	-	-	30	-	-	20	86	89	-	-	-	-	-		
12	trans-	[PdCl <sub>2</sub> py <sub>2</sub> ]	5	-	94	-	-	-	-	26	-	-	16	83	93	-	-	-	-	-		
13	cis-	[PtCl <sub>2</sub> qu <sub>2</sub> ]	6	31	-	-	-	-	-	-	-	-	23	69	-	78	-	-	-	-		
14	trans-	[PtCl <sub>2</sub> qu <sub>2</sub> ]	6	27	-	-	-	-	-	-	-	-	7	13	-	81	-	-	-	-		
15	cis-	[PtCl <sub>2</sub> py <sub>2</sub> ]	7	74	-	-	-	-	-	10	-	-	-	-	-	-	58	-	-	-		
16	trans-	[PtCl <sub>2</sub> py <sub>2</sub> ]	7	97	-	-	-	-	-	19	-	-	-	-	-	-	67	-	-	-		
17	cis-	[Pt(NH <sub>3</sub> ) <sub>2</sub> hx <sub>2</sub> ] <sup>2+</sup>	8	-	52	-	-	82	70	-	-	-	27	-	-	84	-	-	-	-		
18	trans-	[Pt(NH <sub>3</sub> ) <sub>2</sub> hx <sub>2</sub> ] <sup>2+</sup>	8	-	58	-	-	85	74	-	-	-	-	-	-	90	-	-	-	-		
19	cis-	[Pt(Pφ <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	9	-	-	-	-	-	-	85	84	-	-	8	-	-	-	-	-	-		
20	trans-	[Pt(Pφ <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	10	-	-	-	-	-	-	94	88	-	-	23	-	-	-	-	-	-		
21	cis-	[Pt(NH <sub>3</sub> ) <sub>2</sub> py <sub>2</sub> ] <sup>2+</sup>	11	-	26	-	-	49	45	-	-	-	-	-	-	-	-	-	-	-		
22	trans-	[Pt(NH <sub>3</sub> ) <sub>2</sub> py <sub>2</sub> ] <sup>2+</sup>	11	-	18	-	-	31	35	-	-	-	-	-	-	-	-	-	-	-		

\* Abbreviations as in Table III.

\*\* The compositions of solvent systems 15-28 are given in Table II.

\*\*\* Abbreviations as in Table III.

## DISCUSSION

The effect of the geometrical isomerism of square-planar metal complexes on their thin-layer chromatographic behaviour has been studied in a few instances<sup>12-16</sup>, and it has been established that in most instances the *trans* isomers exhibit higher  $R_F$  values than the corresponding *cis* isomers. Therefore, Kauffman *et al.*<sup>14</sup> proposed that in the determination of geometrical isomerism of square-planar complexes thin-layer chromatography should be used in combination with some other suitable method.

However, on the basis of our results, it can be concluded that when single-component solvent systems are used, all the investigated *trans* isomers exhibit higher  $R_F$  values than the corresponding *cis* isomers, whereas when multi-component solvent systems are used in some instances a reverse order is observed. Hence, there is a new possibility for the determination of the geometrical isomerism of square-planar complexes, which is analogous to our earlier reported method<sup>1</sup> for octahedral complexes.

On the basis of the results obtained, we have also elucidated the mechanism involved in these separations. When single-component solvent systems are used the mechanism probably involves sorption, whereas with multi-component solvent systems partition is also possible. Hence, the order of the  $R_F$  values of geometrical isomers will depend on which of these separation mechanisms prevails. This might also explain why in some instances deviations were observed from the regularity that Kauffman *et al.*<sup>14</sup> established for square-planar complexes.

## ACKNOWLEDGEMENTS

The authors are grateful to the Serbian Republic Research Fund for financial support and to Dr. Ružica Tasovac and Mrs. Zorica Lukanić for elemental micro-analyses.

## REFERENCES

- 1 M. B. Čelap, G. Vučković, M. J. Malinar, T. J. Janjić and P. N. Radivojša, *J. Chromatogr.*, 196 (1980) 59.
- 2 G. B. Kauffman and D. D. Cowan, *Inorg. Synth.*, 7 (1963) 239.
- 3 H. D. K. Drew, F. W. Pinkard, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, (1932) 988.
- 4 A. A. Grinberg, *Izv. Inst. Izuch. Plat.*, 6, No. 5 (1928) 122.
- 5 F. Krauss and F. Brodkorb, *Z. Anorg. Chem.*, 165 (1927) 76.
- 6 E. G. Cox, H. Saenger and W. Wardlaw, *J. Chem. Soc.*, (1932) 2216.
- 7 G. B. Kauffman, *Inorg. Synth.*, 7 (1963) 249.
- 8 L. A. Tschugaev and I. I. Tschernjaev, *J. Chem. Soc.*, (1918) 884.
- 9 L. Malatesta and C. Cariello, *J. Chem. Soc.*, (1958) 2323.
- 10 S. H. Mastin and P. Haake, *J. Chem. Soc., Chem. Commun.*, (1970) 202.
- 11 H. D. K. Drew, F. W. Pinkard, W. Wardlaw and E. G. Cox, *J. Chem. Soc.*, (1932) 1004.
- 12 L. F. Druding and S. I. Shupack, *J. Chromatogr.*, 24 (1966) 491.
- 13 G. B. Kauffman and B. W. Benson, *Inorg. Chem.*, 6 (1967) 411.
- 14 G. B. Kauffman, B. H. Gump and B. J. Stedjee, *J. Chromatogr.*, 118 (1976) 433.
- 15 R. L. Dutta, R. K. Ray and G. B. Kauffman, *Coord. Chem. Rev.*, 28 (1979) 23.
- 16 G. B. Kauffman, R. K. Masters, J. C. Bailar, Jr., P. R. Schabinger and M. J. Sinwell, *J. Chromatogr.*, 170 (1979) 209.