

CHROM. 8899

Note

Separation of inorganic isomers by thin-layer chromatography

III. Square planar geometric isomers

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In the first publication in this series¹, we described the separation by thin-layer chromatography (TLC) on silica gel of a number of square planar non-electrolytic geometric isomers of platinum(II) that we had separated previously by column chromatography² along with the separation of two pairs of non-electrolytic binuclear platinum(II) isomers for which column chromatography had proven unsuccessful. In our second paper³, we extended our TLC separations to include a number of different types of octahedral geometric isomers of various metals. In the present paper we report the TLC separation of a number of non-electrolytic as well as electrolytic square planar geometric isomers of other metals in addition to platinum, including the three isomers of [Pt(NH₃)(py)(Br)(NO₂)]. Inasmuch as we demonstrated in our first article¹ that separations can be carried out quantitatively and with significant amounts of material (*ca.* 200 mg of total mixture), all the separations reported here are strictly qualitative. In addition to using mixtures prepared from pure isomers, we also applied the method to materials that should theoretically exist in more than one isomeric form.

EXPERIMENTAL

Isomer samples were kindly provided by the persons listed alphabetically under Acknowledgements (designated by initials in Table I). All eluents were C.P. or reagent grade. Generous samples of the adsorbents used, SilicAR[®] TLC-7F and TLC-7G, were provided by Mallinckrodt (St. Louis, Mo., U.S.A.). Microscope slides (75 × 25 mm) were used for all separations except for sample 8 (Table I) which required 200 × 50 mm plates to achieve separation. Plates were developed by the ascending technique, and iodine vapor was used for visualization. The thiosemicarbazide complexes (samples 5-7) could also be detected by spraying the developed plates with FeCl₃ solution. Further details are given in previous articles¹⁻³.

RESULTS AND DISCUSSION

The results obtained are summarized in Table I. *R_F* values were reproducible to ± 0.03. Although many developing solvents and mixtures were evaluated, only the

TABLE I
THIN-LAYER CHROMATOGRAPHY OF TETRACOORDINATE GEOMETRIC ISOMERS
Abbreviations of sources: see Acknowledgements.

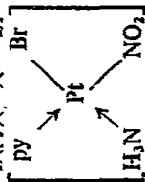
No.	Isomer	Source	Developing solvent	R_F		ΔR_F	Type of separation
				<i>cis</i>	<i>trans</i>		
<i>Type M₂BC</i>							
1	[Ir(PPh ₃) ₂ (CO)Cl] ⁺ one form (lemon yellow)	B.W.M. ⁴	Benzene	0.00	0.61	0.61	Complete
<i>Type M(AB)₂</i>							
2	[Pt(glycinate) ₂] <i>trans</i> (white); <i>cis</i> (white)	F.J. ⁵	Methanol-dichloromethane (1:1)	0.61	0.85	0.24	Partial (smearing of spots)
3	[Cu(tyrosinate) ₂] <i>trans</i> (L) (dark blue); <i>cis</i> (DL) (blue-violet)	F.J. ⁶	Methanol-water (1:1)	0.4-1.0 (considerable tailing)	0.63	?	Partial
4	[Ni(CH ₃) ₂ N ⁺ CH ₂ (=NOH)-C(CH ₃)=NO ₂] ^{*,**} <i>cis-trans</i> mixture; <i>trans</i> (orange); <i>cis</i> (red)	E.U. ⁷	<i>n</i> -Hexane or dichloromethane	—	—	—	None
5	[Ni(thiosemicarbazide) ₂] [†] ·R.A.H. ⁸ <i>cis</i> - and <i>trans</i> -SO ₄ ; <i>cis</i> - and <i>trans</i> -(NO ₂) ₂ ; <i>trans</i> -Cl ₂		(a) Acetone-water (1:1) (b) Methanol-water (1:1) (c) water (d) Dissolved in C ₇ H ₈ , developed in water	0.82; (NO ₂) ₂ (pink-red) 0.00; SO ₄ (red-brown) 0.74; SO ₄ (red-brown) Variable; (NO ₂) ₂ (pink-red)	0.62; SO ₄ ·3 H ₂ O (brown) 0.15; Cl ₂ (greenish brown) 0.00; SO ₄ ·3 H ₂ O (brown) Variable; Cl ₂ (greenish brown)	0.20 0.15 0.74 —	Complete Complete Partial (tailing) Partial (partition chromatography)

NOTES

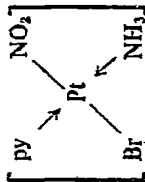
6	$[\text{Pt}(\text{thiosemicarbazide})_2]^{2+}$ R.A.H. ^a <i>trans</i> -Cl ₂ (light yellow); <i>cis</i> -SO ₄ (light orange)	Water	0.60	0.50	0.10	Partial
7	$[\text{Pd}(\text{thiosemicarbazide})_2]^+$ <i>cis</i> -(NO ₂) ₂ ; <i>cis</i> -SO ₄ ; <i>trans</i> -Cl ₂	(a) Acetone-water (1:1) (b) Various solvents	0.00; (NO ₃) ₂ (yellow-orange) SO ₄ ; decomposes (yellow)	0.36; Cl ₂ (yellow) Cl ₂ ; decomposes (yellow)	0.36	Partial (considerable tailing) None

Type MABCD

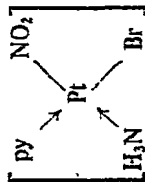
8 $[\text{Pt}(\text{NH}_3)(\text{py})(\text{Br})(\text{NO}_2)]$ A.D.C.^b
(very pale yellow)



(b) $[\text{Pt}(\text{NO}_2)(\text{NH}_3)(\text{Br})]$ (yellow)



(c) $[\text{Pt}(\text{NO}_2)(\text{py})(\text{H}_3\text{N})(\text{Br})]$ (pale yellow)



* Previously separated by column chromatography¹⁰.

** These compounds have since been found to be coordination polymers rather than *cis-trans* isomers¹².

most successful combinations, *i.e.* those resulting in maximum differences between R_F values and minimum tailing, are shown. The following samples, listed by type and number, were successfully separated: $MA_2BC:1$; $M(AB)_2:2$ and 3 (partial), 5(a) and (b), 5(c) and (d) (partial), 6 and 7(a) (partial); and $MABCD:8$. The remaining samples (4, 7(b), 9, and 10) could not be separated. We have previously separated samples 1 and 4 by column chromatography on Al_2O_3 . With several exceptions (samples 3, 5(a), 5(c), and 6), R_F values for the *trans* isomer are greater than those for the *cis* isomer.

CONCLUSIONS

The advantages of TLC in the separation of isomers has been discussed in previous papers^{1,3}. In column chromatography, with only a few exceptions, the *trans* isomer is more mobile than the *cis* isomer and is therefore eluted first¹¹. In TLC, on the other hand, while we have likewise generally found the *trans* isomer to be more mobile, *i.e.* $R_F \text{ trans} > R_F \text{ cis}$, exceptions to this general rule appear to be more numerous and may even depend upon the developing solvent (sample 5). Therefore, while TLC behavior may have some value in proof of configuration, it should be used with more caution than column chromatography and should always be supplemented by other data.

ACKNOWLEDGEMENTS

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