

CHROM. 16,157

Note

Effect of the geometrical configuration of metal complexes on their R_F values obtained by paper chromatography

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(Received July 20th, 1983)

In a study on the effect of the geometrical configuration of cationic metal complexes of cobalt(III), chromium(III) and platinum(II) on their R_F values obtained by paper chromatography, Stefanović and co-workers¹⁻³ established that the *cis*-isomers exhibited higher R_F values than the corresponding *trans*-isomers. An exception to this rule were the R_F values obtained with solvent systems containing phenol. Later, it was found that this rule is valid also for complexes of anionic and neutral types⁴. In the aforementioned studies¹⁻⁴ this rule was confirmed with more than 20 pairs of *cis-trans*-isomeric complexes, the chromatographic separation of which was performed by the use of about 100 solvent systems.

However, some of the subsequent papers have reported data which are inconsistent with the above rule. These studies may be divided into two groups: in the first group the effect of the *cis-trans* geometrical configuration on the R_F values was investigated^{5,7,8}, whereas all other investigations may be placed in the second group⁶. Since different chromatographic techniques and different detection reagents were applied, and the experiments were carried out at different temperatures, we decided to determine the corresponding R_F values by applying the same chromatographic procedure as in our previous studies¹⁻³. However, instead of the chromatographic paper of type "B" provided by the Leningrad factory, which was used by Konunovna⁷, we used Whatman No. 1 paper.

EXPERIMENTAL

Preparation of complexes

All the investigated complexes were synthesized according to previously reported procedures (Table I).

Chromatographic investigation

Chromatography was carried out in a glass cylinder (diameter 20 cm, height 33 cm), by the ascending method, on 3-cm wide paper strips. The solvent was placed into the cylinder 1 h before chromatographic separation; it travelled about 15 cm. The experiments were performed at room temperature, *i.e.*, 21-23°C. Individual isomers and their mixtures were chromatographed in the same cylinder. The detection

TABLE I

 R_F VALUES OF THE INVESTIGATED COMPLEXES

en = Ethylenediamine; DH = dimethylglyoximate; gly = glycinate.

No.	Complex	Ref.	Solvent systems (v/v)	$R_F \times 100$					
				Literature data			Our data		
				cis	trans	ref.	cis	trans	
1	[Co(NH ₃) ₄ (NO ₂) ₂]Cl	(6, 11)	Acetone-0.1 M acetic acid (1:1)	79	81	5*	80	64	
2	[Co(en) ₂ Cl ₂]Cl	(6, 9)	Acetone-0.1 M acetic acid (1:1)	88	91	5*	82	82	
3	[Co(en) ₂ Cl(SCN)]Cl	(9, 10)	Acetone-0.1 M acetic acid (1:1)	87	90	5*	88	88	
4	[Co(en) ₂ Cl(NO ₂)]Cl	(9)	Acetone-0.1 M acetic acid (1:1)	83	87	5*	85	85	
5	[Co(NH ₃) ₄ (NO ₂) ₂]Cl	(6, 11)	Diethyl ether-methanol-conc. HCl-water (50:30:2:20)	23	74	6**	53	37	
6	[Co(NH ₃) ₄ (NO ₂) ₂]NO ₃	(11, 12)	Diethyl ether-methanol-conc. HCl-water (50:30:2:20)	46	60-62	7	44	25	
7	[Co(en) ₂ (NO ₂) ₂]I	(13)	Propanol-isobutanol-water-ammonia (sp. gr. = 0.93) (80:40:80:3)	22	28-31	7	38	32	
8	[Co(DH) ₂ (OH) ₂]NO ₃	(14, 15)	Propanol-isobutanol-water-ammonia (sp. gr. = 0.93) (80:40:80:3)	30	47	7	19	48	
9	[Cu(gly) ₂]	(16, 17)	Water-methanol (40:60)	60	62	8	74	74	
			Water-methanol (70:30)	81	82	8	90	90	
			Water-acetone (70:30)	74	75	8	86	86	
			Water-acetone (80:20)	75	77	8	88	88	
			Water-acetone (90:10)	79	80	8	92	92	
			Water-dioxan (60:40)	69	70	8	86	86	
			Water-dioxan (80:20)	79	80	8	94	94	

of cobalt(III) and copper(II) complexes was performed by dipping the developed dry papers into 2 M ammonium sulphide solution; platinum(II) complexes were detected by spraying the paper strips with 4 M sodium formate solution and then heating at 120°C till the appearance of brown spots.

The R_F values were determined in the usual way, *i.e.*, by dividing the distance of the centre of gravity of each zone from the starting line by the distance of the solvent front from the starting line. The R_F values of individual isomers were consistent with those obtained when mixtures of both isomers were chromatographed in all the cases where the separation of isomers could be achieved. The R_F values given in Table I represent mean values from three experiments.

The electrophoresis experiments were performed by means of an Electro-phoresis Power Supply MA 8902, using Whatman No. 1 filter-paper strips (3 × 33 cm), and 0.8% NH₄Cl as electrolyte solution. The analysis time was *ca.* 6 h, the applied voltage 100 V and the current density 10–20 mA.

RESULTS AND DISCUSSION

On the basis of the R_F values shown in Table I we conclude that the application of the solvent systems cited gives rise either to the same R_F value for both isomers (2-4, 9), or the *cis*-isomers exhibit higher R_F values than do the corresponding *trans*-

isomers (1, 5-7), which is in accordance with the rule established by Stefanović and co-workers¹⁻³. The only exception is the R_F values obtained for the *cis-trans*-isomers of the complex $[\text{Co}(\text{DH})_2(\text{OH}_2)_2]\text{NO}_3$, where DH = dimethylglyoximate. However, these complexes are diprotic acids which on protolysis give hydroxo-aqua and dihydroxo complexes¹⁴. It follows that these isomers are probably changed chemically in the course of the chromatographic separation, and therefore it is uncertain to which compounds the chromatographic spots belong. This is in accordance with the results obtained by electrophoresis, *i.e.*, during this experiment both isomers hardly move from the starting line during the same time, 6 h, *cis*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{NO}_3$, where en = ethylenediamine, moves about 5.1 cm towards the cathode.

There is also an important structural difference between the isomers of the dimethylglyoximate complexes in that, in contrast to the *cis*-isomer, the *trans*-isomer contains two relatively strong hydrogen bonds between the two dimethylglyoximate ligands, which practically convert the two later bidentate ligands into a quadridentate ligand of the porphyrin type¹⁸, and might be the cause of the reversal of the order of R_F values of these isomers.

As regards the diglycinatocopper(II) complex, it is worth mentioning that in some cases Jursik⁸ reported higher R_F values (up to 0.02 R_F units) for the *trans*-isomers (data given in Table I), whereas in other cases he found somewhat higher values for the *cis*-isomer (up to 0.14 R_F units). In these cases, the R_F values were not measured using the distance of the corresponding zone centres of gravity from the starting line, but as the mean distance between the front and the end of the spots from the starting line, which renders the R_F values highly dependent on the spot size. In contrast in all our experiments we obtained the same R_F values for both isomers, using not only the solvent systems cited in Table I but also many others. This is in agreement with the results obtained by O'Brien¹⁹, who found a rapid equilibrium between the isomers in aqueous solution.

Finally, it should be mentioned that the investigations carried out so far here not included either square-planar complexes, except $[\text{Pt}(\text{NH}_3)_2(\text{py})_2]\text{Cl}_2$ ¹⁻³, where py = pyridine, or octahedral complexes of facial or meridional configuration, which will be the subject of further investigations.

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 microanalyses.

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