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Short communication

Thin-layer chromatography of *facial* and *meridional* isomers of Co(III) and Cr(III) complexes on polyacrylonitrile sorbent

Ž.Lj. Tešić^{a,*}, T.J. Sabo^a, S.R. Trifunović^b, D.M. Milojković-Opsenica^a^aFaculty of Chemistry, University of Belgrade, P.O. Box 158, 11001 Belgrade, Yugoslavia^bFaculty of Science, Department of Chemistry, P.O. Box 60, 34001 Kragujevac, Yugoslavia

Abstract

The effect of *facial–meridional* geometrical isomerism of metal complexes on their chromatographic behaviour on a thin layer of polyacrylonitrile sorbent was examined. To that purpose the three following series of complexes were chromatographed: [Co(eddp)Am], where eddp is ethylenediamine-N,N'-3-propionato ligand, Am is glycinate, alaninate, valinate, leucinate, isoleucinate or isobutyrate ligands, [CoAm₃], where Am is glycinate, β-alaninate, valinate or leucinate ligands as well as two pairs of isomer complexes of [Macacphac₃] type, where M is Co(III) or Cr(III) and acacphac is 1-phenyl-1,3-butanedionate ion. For their chromatographic separation four mono- and thirteen polycomponent solvent systems were used. In all the examined cases *meridional* isomers were found to exhibit higher hR_F values than corresponding *facial* isomers. Finally, some possible separation mechanisms are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In several papers to date, the effect of *facial–meridional* isomerism of Co(III) and Cr(III) complexes on their behaviour under planar chromatography conditions has been considered [1–3]. It has been established that *meridional* (*mer*) isomers, analogous to *cis–trans* geometrical isomers on the thin layer of silica gel using monocomponent solvent systems, are more mobile than corresponding *facial* (*fac*) isomers. Contrary to that, by using polycomponent solvent systems in a number of cases a reverse order was found. However, in paper chromatographic separations it has been established that *facial–meridional* isomers behave contrary to *cis–trans* isomers. Namely, by using solvent systems free of strong

mineral acids, *meridional* isomers were found to exhibit higher hR_F values than the corresponding *facial* ones. The deviation from the above mentioned regularity has been established in the cases when a strong acid was used as an electrolyte.

In this work we tried to examine the effect of *facial–meridional* isomerism of a greater number of complexes on their chromatographic behaviour on a thin layer of polyacrylonitrile (PAN) sorbent. This sorbent has been used so far in the separation of the following substances: *cis–trans* isomers of Co(III) complexes [4], foodstuff dyes [5], tris(β-diketonato) complexes of transition metals [6], tris(alkylxanthato)cobalt(III) complexes [7], aliphatic and aromatic amines [8], as well as mixed aminocarboxylato cobalt(III) complexes [9]. By considering the aforementioned sorbent, due to its moderate polarity and surface bifunctionality, it can carry out various

*Corresponding author.

specific and nonspecific interactions with substances being separated, that is, it can be favourable in both normal- and reversed-phase chromatography. Since the effect of *facial–meridional* isomerism of the transition metal complexes on their chromatographic behaviour on a thin layer of PAN sorbent has not been studied so far, ten pairs of aminocarboxylato and two pairs of β -diketonato isomer complexes have been chosen to be investigated in this work.

2. Experimental

All the investigated complexes were synthesized according to the procedures described in the literature [10–17]. The preparation of PAN sorbent, its application to microscopic slides and the development of chromatogram was performed according to the earlier described procedure [4]. For all separations the chromatographic plates were spotted with 2 μ l aliquots of freshly prepared solutions (2 mg/cm³) of the complexes. After development, the coloured spots of the complexes were readily visible. All components of chromatographic solvents used (Table 1) were of analytical grade.

3. Results and discussion

As can be seen from Table 2, for the investigation

Table 1
Compositions of the solvent systems used

No.	Solvent system	Volume ratio
1	Methanol	
2	Ethanol	
3	Ethylene glycol monoethyl ether	
4	Cyclohexane	
5	Methanol–water	90:10
6	Methanol–water	80:20
7	Ethanol–water	90:10
8	Ethanol–water	80:20
9	Ethanol–benzyl alcohol	80:20
10	Ethanol–phenol	80:20
11	Isopropanol–water	80:20
12	Acetone–water	80:20
13	<i>n</i> -Hexane–benzene	80:20
14	<i>n</i> -Hexane–carbon tetrachloride	75:25
15	Cyclohexane–acetone	90:10
16	Acetone–water	70:30
17	Tetrahydrofuran–water	70:30

of the effect of *fac–mer* isomerism of Co(III) complexes on their chromatographic behaviour, two series of complexes are chosen. The first series includes six pairs of isomer complexes of *uns–cis*[Co(eddp)Am] type, where eddp is ethylenediamine-N,N'-3-propionato ligand, Am is glycinate, alaninate, valinate, leucinate, isoleucinate or aminoisobutyrate ligands, while the second series is made up of four pairs of isomers of tris(aminocarboxylato)–Co(III) complexes.

3.1.1. Complexes of *uns–cis*[Co(eddp)Am] type

hR_F values of the above series of complexes obtained by using three mono- and eight dicomponent solvent systems are given in Table 2. As it can be seen from the obtained results, in all cases it was established that *meridional* isomers of the examined complexes have higher hR_F values than corresponding *facial* ones. It is in agreement with the results obtained by chromatographic separation of the same complexes on a thin layer of silica gel, as well as with the results of the separation on paper with strong-acid free solvent systems [3]. In addition, such a chromatographic behaviour of *fac–mer* isomers is analogous to the earlier established behaviour of *cis–trans* isomers under TLC conditions of PAN sorbent [4].

From the obtained results it can also be seen that the branch side of aminocarboxylato series enlargement, as in the case of silica gel, does not lead to the regularity in hR_F value changes which was established by the separation of these complexes on paper [3].

By using the above mono- and dicomponent solvent systems the hR_F values ratio was not changed, but a greater separation selectivity, i.e., a greater discrepancy in hR_F values of *facial* and *meridional* isomers is noticed if the separation is carried out by pure alcohol than by mixtures of alcohol and water. It can also be seen from the ΔhR_F values of the examined isomer complexes obtained by using the corresponding solvent systems (Table 3).

In addition, a greater selectivity is noticed when these complexes are separated on PAN sorbent compared to the selectivity achieved by chromatographic separation of the same series of complexes on silica gel and paper [3]. Namely, the highest selectivity on PAN sorbent is achieved by using

Table 2
 hR_F values of the investigated aminocarboxylato complexes

No.	Complex ^a	Isomer	Ref.	Solvent system ^b											
				1	2	3	5	6	7	8	9	10	11	12	
1	[Co(eddp)gly]	<i>fac</i>	[10]	8	13	21	60	64	52	65	0	0	36	37	
		<i>mer</i>		65	72	72	80	88	85	87	71	54	80	83	
2	[Co(eddp)ala]	<i>fac</i>	[11]	11	15	24	67	75	60	61	10	0	43	60	
		<i>mer</i>		65	69	52	83	89	80	83	69	66	76	90	
3	[Co(eddp)aibu]	<i>fac</i>	[12]	19	22	38	68	75	65	72	21	0	57	67	
		<i>mer</i>		53	62	72	95	97	77	78	58	79	76	77	
4	[Co(eddp)val]	<i>fac</i>	[11]	14	17	31	62	64	46	58	14	0	29	57	
		<i>mer</i>		62	67	56	89	90	63	77	52	50	64	83	
5	[Co(eddp)leu]	<i>fac</i>	[11]	17	17	34	57	61	44	55	17	0	27	53	
		<i>mer</i>		59	66	64	79	92	70	75	68	71	72	80	
6	[Co(eddp)ileu]	<i>fac</i>	[11]	14	20	24	55	57	44	52	16	0	36	50	
		<i>mer</i>		56	55	62	77	78	67	62	48	73	70	60	
7	[Co(gly) ₃]	<i>fac</i>	[13]	0	8				0	9	0				
		<i>mer</i>		62	57				59	76	21				
8	[Co(β-ala) ₃]	<i>fac</i>	[14]	0	43				38	55	15				
		<i>mer</i>		83	87				80	85	75				
9	[Co(val) ₃]	<i>fac</i>	[15]	47	75				77	89	62				
		<i>mer</i>		85	89				87	94	79				
10	[Co(leu) ₃]	<i>fac</i>	[15]	82	77				90	90	74				
		<i>mer</i>		88	90				96	96	81				

^a eddp – ethylenediamine-N,N'-3-propionato ligand; glyH – glycine; alaH – L-alanine; aibu – α-aminoisobutyric acid; valH – L-valine; leuH – L-leucine; ileuH – L-isoleucine.

^b See Table 1.

ethanol as a solvent, i.e., $\overline{\Delta hR_F} = 48$, while for silica gel and paper the values were 18.7 and 18.2, respectively.

With regard to the mechanism of the above-mentioned separations, some parameters point to normal-phase behaviour of the examined complexes. Namely, whether normal-phase or reversed-phase chromatography is in question, could be estimated on the

basis of the data obtained, which is the effect of the change of the water content in the solvent system on the retention of the substances being separated [18]. Thus, in normal-phase chromatography an increase in water contents results in an increase in hR_F values of separating substances. Such a behaviour is established in this work also by comparing hR_F values obtained by pure alcohol and the mixtures of alcohol

Table 3
 ΔhR_F values^a of investigated complexes

Complex ^b	Solvent ^c						
	1	2	5	6	7	8	
[Co(eddp)Gly]	57	59	22	33	24	20	
[Co(eddp)Ala]	54	54	22	20	14	16	
[Co(eddp)α-aibu]	34	40	12	6	22	27	
[Co(eddp)Val]	48	50	19	17	26	7	
[Co(eddp)Leu]	42	49	20	26	31	22	
[Co(eddp)Ileu]	42	35	10	23	20	23	
ΔR_F	46	48	18	21	23	19	

^a $\Delta R_F = (R_F)_{mer} - (R_F)_{fac}$

^b See Table 2.

^c See Table 1.

and water in volume ratios of 90:10 and 80:20 (Table 2, solvents 1,2; 5–8).

On the other hand, salting-out chromatography, as a typical reversed-phase method, could not be used, because the addition of an electrolyte, regardless of its concentration, resulted in motion of the complexes under examination with the front of the solvent.

Due to the occurrence of electronegative nitrogen and oxygen atoms in the complexes and nature of sorbent surface, it could be assumed that the sorption of these compounds on PAN sorbent is based on hydrogen bonds between the donor atoms of the complexes and methyne hydrogen atoms of the sorbent. A stronger sorption of the examined *facial* isomers could be explained, as in the case of silica gel [3], by a favourable location of electronegative atoms of the complex in forming hydrogen bonds with the sorbent. Namely, due to the existence of three electronegative atoms on one of octahedral faces the *facial* isomer can form three hydrogen bonds with sorbent, unlike the *meridional* isomer that can form only two such bonds.

Considering the strength of the hydrogen bonds on silica gel and PAN sorbent, a weaker sorption of the above complexes was noticed on the latter sorbent. Namely, the use of the solvent system with higher water content, as used in chromatography on silica gel [3], in the case of PAN sorbent resulted in motion of the complex with front of the solvent. This is apparent, because the methyne hydrogen of PAN sorbent, due to the difference in electronegativity of carbon and oxygen, forms a weaker hydrogen bond with donor atoms of the complex than does the hydrogen atom of the silanol group.

3.1.2. Tris(aminocarboxylato)–Co(III) complexes

Besides the mixed aminocarboxylato–Co(III)

complexes already described, four pairs of *fac*–*mer* isomers of tris(aminocarboxylato)–Co(III) complexes were chromatographed in this work. The hR_F values obtained are given in Table 2.

As it can be seen from the results, in all the examined cases it has been established that *meridional* isomers exhibit higher hR_F values than those of the corresponding *facial* ones. In addition, the enlargement of the number of carbon atoms in the aminocarboxylato ligand in all cases lead to a decrease in the retention of the corresponding complexes. This fact is in agreement with the earlier established effect of the length of side ligand series on the behaviour of transition metal complexes under the condition of normal-phase chromatography [3].

Considering the presence of the same number and type of donor atoms, as in the case of the complex of *uns-cis*[Co(eddp)Am] type, and the analogous chromatographic behaviour, the sorption by hydrogen bond formation between sorbent and sorbent could be assumed as a predominant separation mechanism in this case.

3.1.3. Tris(β -diketonato) complexes

The effect of *fac*–*mer* isomerism on the chromatographic behaviour of transition metal complexes on a thin layer of PAN sorbent, was also considered by chromatographing two pairs of isomer complexes of [M(phacacac)₃] type, where M is Co(III) or Cr(III) and phacacac is 1-phenyl-1,3-butanedionato ligand. The hR_F values obtained by means of four nonaqueous and two aqueous solvent systems are given in Table 4.

As can be seen from these results, it has been established, in this case as well, that *meridional* isomers exhibit higher hR_F values than corresponding *facial* ones.

Table 4
 hR_F values of the investigated β -diketonato complexes

No.	Complex ^a	Ref.	Isomer	Solvent system ^b					
				4	13	14	15	16	17
1	[Co(acacPhac) ₃]	[16]	<i>fac</i>	0	0	0	10	23	51
			<i>mer</i>	11	16	22	38	62	66
2	[Cr(acacPhac) ₃]	[17]	<i>fac</i>	0	29	13	32	38	55
			<i>mer</i>	7	37	23	44	64	71

^a acacphac-1-phenyl-1,3-butanedionato ion.

^b See Table 1.

In view of our earlier work [6], where it was shown that the separation of this type of complexes on a thin layer of PAN sorbent was based on donor–acceptor interactions of the π -electronic systems of complexes with sorbent cyano groups, a stronger retention of *facial* isomers could be explained by a more favourable orientation of their aromatic rings in realizing these interactions compared to *meridional* isomers.

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