Journal of Chromatography, 196 (1980) 59–74
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 12,844

EFFECT OF THE COMPOSITION AND STRUCTURE OF COBALT(III) COMPLEXES ON THEIR R_F VALUES OBTAINED BY THIN-LAYER CHROMATOGRAPHY ON SILICA GEL

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(Received March 18th, 1980)

SUMMARY

Thin-layer chromatography on silica gel was used for the chromatographic separation of 75 cobalt(III) complexes using 30 one-, two- and three-component solvent systems. It was observed that when chromatographing with one-component solvent systems, *trans*-isomers exhibit higher R_F values than the corresponding *cis*-isomers. In the other solvent systems some exceptions were observed. A linear dependence between the number of five-membered rings substituted by six-membered rings and their R_M values has been established. Finally, it was found that an increase in the number of carbon atoms in the aminocarboxylato ligand results in an increase in the R_F value of the complex and that there is a linear correlation between this number and the R_M values of the complexes.

INTRODUCTION

In earlier work[1,2] we studied the effect of the composition and the structure of cobalt(III) complexes on their R_F values obtained by paper chromatography. Continuing these investigations in this work, we have carried out a systematic study of the effects of the following factors on the R_F values of the same complexes obtained by thin-layer chromatography: the geometric configuration of the complex, the size of the chelate ring and the size of the branched chain of the coordinated amino acids.

By comparing our earlier results obtained by paper chromatography[1,2] with those obtained in the present work we wanted to establish which of the possible mechanisms prevails in the cases studied. These investigations were carried out with compounds mainly prepared for the first time in our laboratory.

EXPERIMENTAL

Syntheses of the complexes investigated were carried out according to procedures described in the literature (Tables III–VII).

Chromatographic separations were performed by ascending thin-layer chromatography on silica gel G-RS (Carlo Erba, Milan, Italy) which contained 13% of calcium sulphate. A suspension of silica gel (30 g) in water (70 cm^3) was applied on five glass plates (19.5 × 13 × 0.5 cm), which had been washed first with a detergent solution and then with acetone–ethanol (1:1). The layer thickness was 300 μm.

In order to ensure that the layers were uniformly wetted in the course of the development, silica gel pasted along the edges of the plates was removed. The plates were dried in air for 15 min and then heated in a drying cabinet at 110°C for 1 h. After this treatment the plates were kept in a desiccator over anhydrous calcium chloride.

Aqueous solutions of the investigated complexes were applied in the form of small drops. The development was carried out in cylinders (13.5 × 19.5 × 23.5 cm). One hour before the development, the solvent mixture was placed in a cylinder in order to saturate it with solvent vapour. Solvent systems consisting of p.a. grade solvents were used and their compositions are listed in Tables I and II. The solvent systems travelled about 10 cm and detection was performed by spraying the plates with 2 *M* ammonium sulphide solution.

All investigations were performed at 20 ± 2°C.

TABLE I

ONE-COMPONENT SOLVENT SYSTEMS USED

No.	*Component*	*Time of development (min)*
1	Distilled water	15
2	Methanol	15
3	Ethanol	40
4	Ethylene glycol monomethyl ether	55
5	Dimethyl sulphoxide	45
6	N,N-Dimethylformamide	25
7	Acetonitrile	30
8	1,2-Propanediol	16 h
9	1,3-Propanediol	10 h

RESULTS AND DISCUSSION

Effect of geometric configuration on R_F values of the investigated complexes

The investigations were carried out by chromatographing 16 cationic, anionic and neutral cobalt(III) complexes (Tables III and IV). The thin-layer chromatographic behaviour of the most of these complexes had not been investigated previously. Chromatographic development was carried out by using 8 one-component and 14 multi-component solvent systems.

It was established that with one-component systems the *trans*-isomers always exhibit higher R_F values than the corresponding *cis*-isomers (Table III). However, when using multi-component solvent systems, in 35% of cases the *cis*-isomers were more mobile than the corresponding *trans*-isomers (Table IV).

On the basis of the results it was concluded that with one-component solvent systems the predominant process is adsorption or ionic exchange. As silica gel behaves as a weakly acidic cationic exchanger[9] containing silanol groups, we believe that with

TABLE II

MULTI-COMPONENT SOLVENT SYSTEMS USED

No.	*Composition*	*Proportions (v/v)*	*Time of development (min)*
10	Ethanol–methanol	30:70	45
11	Ethanol–methanol	50:50	30
12	Ethanol–methanol	70:30	25
13	Acetic acid–water	80:20	55
14	Pyridine–water	90:10	40
15	α-Picoline–water	50:50	10
16	Acetone–water	85:15	25
17	Acetylacetone–water	40:60	35
18	Acetylacetone–water	50:50	45
19	Formic acid–acetic acid	50:50	55
20	Dioxan–water	90:10	55
21	Dioxan–water–KI	85:15:1 g per 100 ml	60
22	Phenol saturated with 2 *N* HCl	—	100
23	Ethyl acetate–ethanol–water	15:15:70	20
24	Ethyl acetate–ethanol–water	30:20:50	35
25	Ethyl acetate–ethanol–water	50:30:20	40
26	Ethyl acetate–ethanol–water	70:20:10	50
27	Isopropanol–water–conc. HNO_3	70:25:5	120
28	Isopropanol–water–conc. HNO_3	90:5:5	90
29	Acetone–water–conc. HNO_3	75:20:5	30
30	*n*-Butanol–ethanol–water	70:20:10	60

anionic or neutral complexes type hydrogen bonding to silica gel occurs, whereas with cationic complexes type it is likely that ion exchange between the silanol-group hydrogen and the cation also takes place. Moreover, the lower mobility of *cis*-isomers is in accordance with the fact that they are more polar than the corresponding *trans*-isomers and that they are therefore more strongly adsorbed to the adsorbent.

With multi-component solvent systems containing water, in addition to adsorption and ion exchange, the process of partition is inevitable so that the sequence of the isomers on the plates depends on the mechanism that predominates.

By comparing the results obtained by paper chromatography[1,2] with those obtained by thin-layer chromatography for the same cobalt(III) complexes, it can be seen that the composition of multi-component systems has no effect on the sequence of geometrical isomers in the paper chromatographic separation, whereas in the thin-layer chromatographic procedure the sequence of isomers depends on the composition of the solvent system. This may be understood in view of the fact that in paper chromatography the predominant mechanism is that of partition, whereas in thin-layer chromatography separation the predominant mechanism depends on the composition of the multi-component solvent systems.

On the basis of the above, it can be concluded that the so far accepted general rule[10–12] that *trans*-isomers exhibit higher R_F values than the corresponding *cis*-isomers is valid in thin-layer chromatography on silica gel only when one-component solvent systems are used. In addition, we consider that one should differentiate between the results obtained with one-component and multi-component solvent systems. With one-component solvent systems, where sorption is dominating, a regu-

TABLE III

EFFECT OF THE GEOMETRICAL CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR R_F VALUES OBTAINED WITH ONE-COMPONENT SOLVENT SYSTEMS

No.	*Isomer*	*Complex**	*Ref.*	$R_F \times 100$**							
				1	*2*	*3*	*4*	*5*	*6*	*8*	*9*
1	*cis*-NO_2	$[Cotn_2(NO_2)_2]^+$	3	39	3	3	3	14	30	8	7
2	*trans*-NO_2		3	43	9	5	13	16	38	14	18
3	*cis*-NO_2	$[Coen_2(NO_2)_2]^+$	4	54	4	0	3	14	4	7	4
4	*trans*-NO_2		4	58	6	3	5	23	7	13	14
5	*cis*-NO_2	$[Copn_2(NO_2)_2]^+$	5	33	3	0	2	15	—	12	7
6	*trans*-NO_2		5	35	6	3	3	23	—	15	14
7	*cis*-NO_2-*trans*-N	$[Co(\beta\text{-ala})_2(NO_2)_2]^-$	6	—	—	51	85	—	82	—	—
8	*trans*-*trans*-*trans*		6	—	—	55	91	—	89	—	—
9	*cis*-NO_2-*trans*-NH_2, NH_3	$[Co(NH_3)_2gly(NO_2)_2]$	7	—	69	18	—	—	81	87	88
10	*trans*-NO_2		7	—	79	24	—	—	85	95	91
11	*cis*-NO_2-*trans*-NH_2	$[Coen(\beta\text{-ala})(NO_2)_2]$	8	83	55	15	60	—	73	69	72
12	*trans*-NO_2		8	90	65	25	71	—	82	81	80
13	*cis*-NO_2-*trans*-NH_2	$[Cotngly(NO_2)_2]$	8	—	72	—	81	—	—	88	84
14	*trans*-NO_2		8	—	75	—	89	—	—	92	88
15	*cis*-NO_2-*trans*-NH_2	$[Cotn(\beta\text{-ala})(NO_2)_2]$	8	71	57	22	60	—	88	71	77
16	*trans*-NO_2		8	79	68	36	78	—	99	86	84

* tn = 1,3-diaminopropane; en = 1,2-diaminoethane; pn = 1,2-diaminopropane; glyH = glycine; β-alaH = β-alanine.

** The compositions of the solvent systems are given in Table I.

TABLE IV

EFFECT OF THE GEOMETRICAL CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR R_F VALUES OBTAINED WITH MULTI-COMPONENT SOLVENT SYSTEMS

No.	*Isomer*	*Complex**	*Ref.*	$R_F \times 100$**													
				10	*11'*	*13*	*14*	*15*	*16*	*18*	*19*	*21*	*22*	*23*	*27*	*28*	*29*
1	*cis*-NO_2	$[Cotn_2(NO_2)_2]^+$	3	2	—	62	—	36	—	59	—	49	47	32	75	43	88
2	*trans*-NO_2		3	5	—	68	—	39	—	67	—	62	53	39	64	31	85
3	*cis*-NO_2	$[Coen_2(NO_2)_2]^+$	4	2	—	70	—	41	—	—	77	37	40	39	75	—	92
4	*trans*-NO_2		4	4	—	64	—	44	—	—	75	58	46	42	59	—	82
5	*cis*-NO_2	$[Copn_2(NO_2)_2]^+$	5	—	2	74	—	39	—	—	85	52	47	29	85	69	92
6	*trans*-NO_2	$[Copn_2(NO_2)_2]^+$	5	—	6	69	—	48	—	—	78	65	53	31	69	46	88
7	*cis*-NO_2-*trans*-N	$[Co(\beta\text{-ala})_2(NO_2)_2]^-$	6	85	79	79	73	—	75	—	81	52	—	—	92	89	—
8	*trans*-*trans*-*trans*		6	87	86	83	79	—	86	—	76	57	—	—	89	81	—
9	*cis*-NO_2-*trans*-NH_3, NH_3	$[Co(NH_3)_2 gly (NO_2)_2]$	7	33	—	83	68	—	82	—	—	80	53	—	—	39	—
10	*trans*-NO_2		7	50	—	79	88	—	76	—	—	87	51	—	—	34	—
11	*cis*-NO_2-*trans*-NH_2	$[Coen(\beta\text{-ala})(NO_2)_2]$	8	41	38	66	54	89	55	80	74	63	—	89	69	45	—
12	*trans*-NO_2		8	53	50	72	66	92	58	83	70	69	—	93	58	32	—
13	*cis*-NO_2-*trans*-NH_2	$[Cotngly(NO_2)_2]$	8	57	—	76	80	—	75	—	—	74	77	—	71	50	—
14	*trans*-NO_2		8	60	—	78	89	—	69	—	—	79	74	—	63	40	—
15	*cis*-NO_2-*trans*-NH_2	$[Cotn(\beta\text{-ala})(NO_2)_2]$	8	49	44	65	66	90	58	73	78	64	88	89	—	—	—
16	*trans*-NO_2		8	61	57	71	84	94	61	80	68	74	81	92	—	—	—

* Abbreviations as in Table III.

** The compositions of the solvent systems are given in Table II.

TABLE V

EFFECT OF THE CHELATE RING SIZE ON R_F VALUES OBTAINED WITH ONE-COMPONENT SOLVENT SYSTEMS

No.	*Isomer*	*Complex**	*Ref.*	$R_F \times 100$**							
				1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
1	—	$[\text{Cogly}(\text{NO}_2)_2]^{2-}$	13	—	—	27	68	—	—	—	—
2	—	(β-ala)	13	—	—	6	13	—	—	—	—
3	*cis*-NO_2-*trans*-N	$[\text{Cogly}_2(\text{NO}_2)_2]^-$	6	—	89	38	79	—	—	—	—
4	*cis*-NO_2-*trans*-N	gly (β-ala)	8	—	87	30	73	—	—	—	—
5	*cis*-NO_2-*trans*-N	(β-ala)$_2$	6	—	85	24	70	—	—	—	—
6	*trans-trans-trans*	$[\text{Cogly}_2(\text{NO}_2)_2]^-$	6	—	89	—	92	—	—	—	—
7	*trans-trans-trans*	(β-ala)$_2$	6	—	87	—	86	—	—	—	—
8	*cis*-O-*trans*-NH_2	$[\text{CoNH}_3\text{gly}_2\,\text{NO}_2]$	7	95	58	37	95	—	—	—	87
9	*cis*-O-*trans*-NH_2	(β-ala)$_2$	7	83	45	10	44	—	—	—	63
10	Meridional (1,2,6)	$[\text{CoNH}_3\text{gly}(\text{NO}_2)_3]^-$	14	—	93	70	—	—	—	20	—
11	Meridional (1,2,6)	(β-ala)	7	—	88	63	—	—	—	7	—
12	*cis*-NO_2-*trans*-NH_2, NH_3	$[\text{Co}(\text{NH}_3)_2\,\text{gly}(\text{NO}_2)_2]$	7	96	66	16	64	—	—	—	92
13	*cis*-NO_2-*trans*-NH_2, NH_3	(β-ala)	7	88	58	13	57	—	—	—	84
14	*cis*-NO_2-*trans*-NH_2	$[\text{Coengly}(\text{NO}_2)_2]$	4	82	58	20	72	—	89	—	87
15	*cis*-NO_2-*trans*-NH_2	(β-ala)	8	75	53	13	60	—	81	—	72
16	*cis*-NO_2-*trans*-NH_2	$[\text{Cotngly}(\text{NO}_2)_2]$	8	76	72	32	85	—	95	7	91
17	*cis*-NO_2-*trans*-NH_2	(β-ala)	8	64	59	18	66	—	80	3	72

18	*trans*-NO_2	[Cotngly $(NO_2)_2$]	8	79	73	28	89	—	—	—	92
19	*trans*-NO_2	(β-ala)	8	73	69	27	83	—	—	—	88
20	*cis*-NO_2	[$Coen_2$ $(NO_2)_2$]$^+$	4	58	16	—	12	10	13	4	—
21	*cis*-NO_2	tn_2	3	40	18	—	7	13	23	1	—
22	*trans*-NO_2	[$Coen_2$ $(NO_2)_2$]$^+$	4	49	24	—	8	—	19	—	8
23	*trans*-NO_2	entn	8	47	30	—	11	—	24	—	11
24	*trans*-NO_2	tn_2	3	44	34	—	13	—	27	—	15
25	Meridional (1,2,6)	[$Cogly_3$]	15	95	32	—	32	86	—	—	81
26	Meridional (1,2,6)	gly_2 (β-ala)	16	90	28	—	25	80	—	—	72
27	Meridional (1,2,6)	$(β\text{-ala})_3$	17	79	23	—	16	76	—	—	46
28	Facial (1,2,3)	[$Cogly_3$]	15	81	—	—	—	—	2	—	—
29	Facial (1,2,3)	$(β\text{-ala})_3$	17	73	—	—	—	—	0	—	—
30	*trans*-N	[$Cooxgly_2$]$^-$	18	—	—	4	35	—	6	—	—
31	*trans*-N	$(β\text{-ala})_2$	19	—	—	9	53	—	12	—	—
32	C_2-*cis*-N	[$Cooxgly_2$]$^-$	18	—	—	13	12	—	7	—	—
33	C_2-*cis*-N	$(β\text{-ala})_2$	19	—	—	17	17	—	13	—	—
34	—	[$Coox_2gly$]$^{2-}$	20	—	—	—	5	—	12	—	—
35	—	(β-ala)	20	—	—	—	7	—	16	—	—

* Abbreviations as in Table III.

** The compositions of the solvent systems are given in Table I.

larity in chromatographic behaviour is to be expected; this regularity offers a possibility for the determination of the geometrical configuration of these complexes. In contrast, when multi-component solvent mixtures are used, the composition of the solvent system controls whether sorption or partition will dominate and therefore the sequence of isomers depends on the composition of the solvent system.

Effect of chelate ring size on R_F values of the investigated complexes

To investigate the effect of the chelate ring size on the R_F values of complex

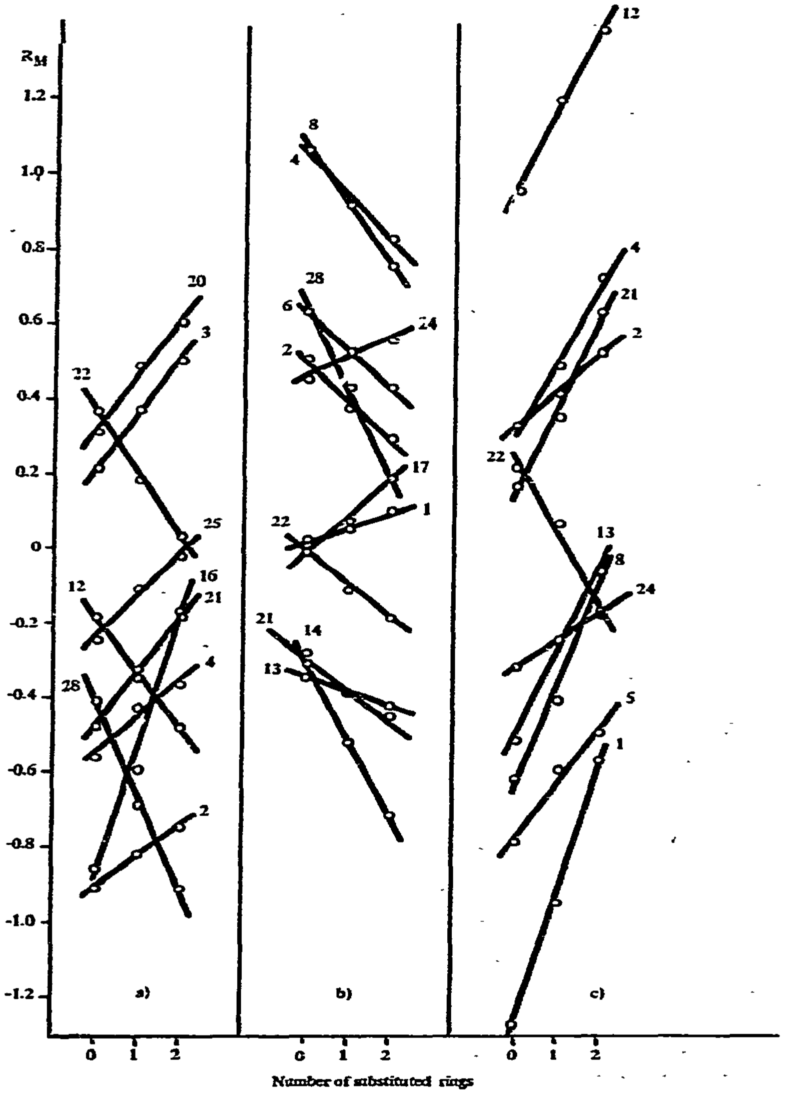

Fig. 1. Dependence of R_M values on the number of five-membered rings substituted by the corresponding six-membered rings. Complexes: (a) 3–5; (b) 22–24; (c) 25–27 (see Tables V and VI). The numbers on the lines refer to the solvent systems used (see Tables I and II).

compounds we chromatographed 35 cobalt(III) complexes (Table V) containing five- and/or six-membered aminocarboxylato and/or diamine chelate ligands. The complexes were cationic, anionic and neutral types. Chromatographic separations were performed using 20 one- and multi-component solvent systems (Tables I and II).

Eleven groups of complex compounds containing aminocarboxylato ligands, either with or without nitro groups, were chromatographed by the use of eight one-component solvent systems (Table V, complexes 1–19 and 25–29); it was found that the R_F value decreased with increasing chelate ring size. Contrary to these findings, three groups of complexes with oxalato chelate rings instead of nitro groups exhibited the opposite behaviour (Table V, complexes 30–35). None of these regularities oc-

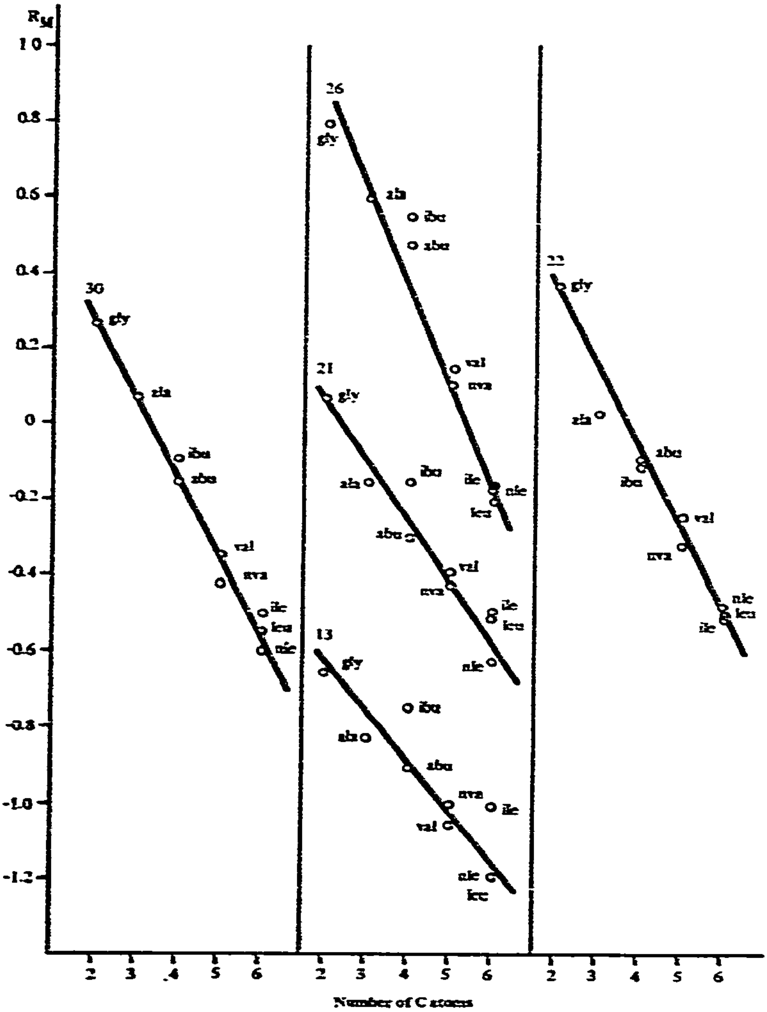

Fig. 2. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the $(+)_{589}$-*cis*(NO_2), *trans*(N)-$[CoAm_2(NO_2)_2]^-$ complex. The numbers on the lines refer to the solvent systems used (see Table II).

TABLE VI

EFFECT OF THE CHELATE RING SIZE ON R_F VALUES OBTAINED WITH MULTI-COMPONENT SOLVENT SYSTEMS

No.	Isomer	Complex*	Ref.	$R_F \times 100$**											
				12	*16*	*14*	*22*	*17*	*11*	*13*	*28*	*21*	*24*	*25*	*20*
1	—	[Cogly $(NO_2)_4]^{2-}$	13	49	—	—	—	—	—	83	—	71	—	51	41
2	—	(β-ala)	13	10	—	—	—	—	—	85	—	78	—	56	36
3	*cis*-NO_2-*trans*-N	[Cogly$_2$ $(NO_2)_2]^-$	6	61	88	—	30	—	—	—	72	75	—	53	33
4	*cis*-NO_2-*trans*-N	gly (β-ala)	8	69	80	—	40	—	—	—	83	68	—	45	25
5	*cis*-NO_2-*trans*-N	(β-ala)$_2$	6	75	60	—	48	—	—	—	89	61	—	40	20
6	*trans-trans-trans*	[Cogly$_2$ $(NO_2)_2]^-$	6	68	86	82	23	—	75	85	41	67	—	10	29
7	*trans-trans-trans*	(β-ala)$_2$	6	74	73	77	45	—	80	80	82	65	—	29	23
8	*cis*-O-*trans*-NH_2	[CoNH$_3$gly$_2$NO$_2$]	7	50	75	92	48	—	54	82	30	57	—	49	29
9	*cis*-O-*trans*-NH_2	(β-ala)$_2$	7	21	23	39	67	—	19	65	55	45	—	17	18
10	Meridional (1,2,6)	[CoNH$_3$gly $(NO_2)_3]^-$	14	82	—	—	33	—	87	—	85	—	—	73	49
11	Meridional (1,2,6)	(β-ala)	7	80	—	—	42	—	84	—	87	—	—	70	23
12	*cis*-NO_2-*trans*-NH_2, NH_3	[Co$(NH_3)_2$ gly$(NO_2)_2$]	7	29	82	77	52	99	—	88	39	76	—	63	52
13	*cis*-NO_2-*trans*-NH_2, NH_3	(β-ala)	7	24	65	67	66	80	—	86	68	64	—	50	40
14	*cis*-NO_2-*trans*-NH_2	[Coengly $(NO_2)_2$]	4	33	64	75	76	—	37	80	49	65	—	—	35
15	*cis*-NO_2-*trans*-NH_2	(β-ala)	8	24	52	61	80	—	33	68	56	54	—	—	29

16	*cis*-NO$_2$-*trans*-NH$_2$	[Cotngly(NO$_2$)$_2$]	8	46	77	87	80	87	54	78	—	74	68	58	55
17	*cis*-NO$_2$-*trans*-NH$_2$	(β-ala)	8	31	58	65	97	48	35	67	—	61	61	44	37
18	*trans*-NO$_2$	[Cotngly(NO$_2$)$_2$]	8	51	73	99	79	80	58	74	36	80	68	48	61
19	*trans*-NO$_2$	(β-ala)	8	46	62	88	91	75	50	72	52	75	54	40	53
20	*cis*-NO$_2$	[Coen$_2$(NO$_2$)$_2$]$^+$	4	—	—	—	50	50	—	64	43	—	15	—	—
21	*cis*-NO$_2$	tn$_2$	3	—	—	—	56	44	—	77	48	—	8	—	—
22	*trans*-NO$_2$	[Coen$_2$(NO$_2$)$_2$]$^+$	4	—	—	67	51	51	—	69	18	66	26	—	—
23	*trans*-NO$_2$	entn	8	—	—	77	57	46	—	71	27	71	23	—	—
24	*trans*-NO$_2$	tn$_2$	3	—	—	84	61	39	—	73	40	74	22	—	—
25	Meridional (1,2,6)	[Cogly$_3$]	15	10	—	—	38	—	—	77	—	41	68	—	—
26	Meridional (1,2,6)	gly$_2$(β-ala)	16	6	—	—	46	—	—	64	—	31	64	—	—
27	Meridional (1,2,6)	(β-ala)$_3$	17	4	—	—	61	—	—	54	—	19	60	—	—
28	Facial (1,2,3)	[Cogly$_3$]	15	6	—	—	30	—	—	—	—	38	—	18	—
29	Facial (1,2,3)	(β-ala)$_3$	17	3	—	—	55	—	—	—	—	16	—	5	—
30	*trans*-N	[Cooxgly$_2$]$^-$	18	32	34	7	13	—	—	76	5	—	—	18	—
31	*trans*-N	(β-ala)$_2$	19	36	36	12	39	—	—	65	34	—	—	10	—
32	C$_2$-*cis*-N	[Cooxgly$_2$]$^-$	18	13	15	6	—	—	—	76	31	—	—	10	—
33	C$_2$-*cis*-N	(β-ala)$_2$	19	17	18	9	—	—	—	78	35	—	—	14	—
34	—	[Coox$_2$gly]$^{2-}$	20	7	—	8	—	—	—	69	25	—	—	6	—
35	—	(β-ala)	20	10	—	12	—	—	—	72	29	—	—	10	—

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[*] Abbreviations as in Table III.

[**] The compositions of the solvent systems are given in Table II.

TABLE VII

EFFECT OF THE NUMBER OF CARBON ATOMS OF AMINOCARBOXYLATO LIGANDS ON R_F VALUES OBTAINED WITH MULTICOMPONENT SOLVENT SYSTEMS

No.	*Isomer*	*Complex**	*Ref.*	$R_F \times 100$**									
				30	*28*	*26*	*14*	*20*	*11*	*22*	*13*	*16*	*21*
1	*cis*-NO_2-*trans*-N	$[Cogly_2(NO_2)_2]^-$	23	35	—	14	—	—	—	35	82	—	46
2	(+)***-*cis*-NO_2-*trans*-N	(L-ala)$_2$	23	46	—	20	—	—	—	48	87	—	59
3	(+)-*cis*-NO_2-*trans*-N	(L-abu)$_2$	24	59	—	25	—	—	—	55	89	—	67
4	(+)-*cis*-NO_2-*trans*-N	(ibu)$_2$	24	55	—	22	—	—	—	57	85	—	59
5	(+)-*cis*-NO_2-*trans*-N	(L-nva)$_2$	24	73	—	44	—	—	—	68	91	—	73
6	(+)-*cis*-NO_2-*trans*-N	(L-val)$_2$	24	69	—	42	—	—	—	64	92	—	71
7	(+)-*cis*-NO_2-*trans*-N	(L-nle)$_2$	24	80	—	60	—	—	—	75	94	—	81
8	(+)-*cis*-NO_2-*trans*-N	(L-leu)$_2$	24	78	—	62	—	—	—	76	94	—	77
9	(+)-*cis*-NO_2-*trans*-N	(L-ile)$_2$	24	76	—	59	—	—	—	77	91	—	76
10	*cis*-O-*trans*-NH_2	$[CoNH_3gly_2NO_2]$	7	25	37	7	—	25	25	55	70	43	42
11	(+)-*cis*-O-*trans*-NH_2	(L-ala)$_2$	7	41	71	14	—	48	64	67	81	62	61
12	(+)-*cis*-O-*trans*-NH_2	(L-abu)$_2$	25	54	84	28	—	67	90	73	90	76	74
13	(+)-*cis*-O-*trans*-NH_2	(L-nva)$_2$	25	68	94	35	—	73	98	75	93	85	81
14	(+)-*cis*-O-*trans*-NH_2	(L-val)$_2$	25	70	94	43	—	81	99	89	95	92	86
15	Meridional (1,2,6)	$[CoNH_3gly(NO_2)_3]$	14	68	88	31	90	—	84	35	—	—	65
16	(—)-Meridional (1,2,6)	L-ala	14	73	92	38	93	—	87	42	—	—	70
17	(—)-Meridional (1,2,6)	L-abu	14	75	95	43	97	—	89	48	—	—	74
18	(—)-Meridional (1,2,6)	L-nva	14	78	97	51	99	—	93	53	—	—	76
19	*cis*-NO_2-*trans*-NH_2, NH_3	$[Co(NH_3)_2gly(NO_2)_2]$	7	24	82	33	81	51	32	49	—	87	68
20	(+)-*cis*-NO_2-*trans*-NH_2, NH_3	L-ala	7	27	86	37	86	64	43	57	—	90	73
21	(+)-*cis*-NO_2-*trans*-NH_2, NH_3	L-abu	7	55	88	47	89	72	60	65	—	93	77
22	*trans*-NO_2-*cis*-NH_3	gly	7	34	33	24	—	—	—	50	82	78	48
23	*trans*-NO_2-*cis*-NH_3	L-ala	7	39	69	33	—	—	—	53	86	84	71
24	*trans*-NO_2-*cis*-NH_3	L-abu	7	45	90	40	—	—	—	56	88	89	81

* L-alaH = L-alanine; L-abuH = L-aminobutyric acid; L-nvaH = L-norvaline; L-valH = L-valine; L-nleH = L-norleucine; L-leuH = L-leucine; L-ileH = L-isoleucine.

** The compositions of the solvent systems are given in Table II.

*** Sign of optical rotation at 589 nm.

curred for the remaining complexes (Table V, complexes 20–24) as well as when multi-component solvent mixtures were used (Table VI).

However, in all instances where the groups contained three complexes each, a linear correlation was found between the number of five-membered rings substituted by the corresponding six-membered rings and the R_M value of the complex (Fig. 1). Contrary to the results obtained by paper chromatography[1], where this correlation was always negative, in thin-layer chromatography on silica gel this correlation was found to be either positive or negative.

Effect of branched chain size of coordinated amino acids on R_F values of the investigated complexes

It is known that in thin-layer chromatography there is a linear correlation between the number of carbon atoms in a homologous series of some organic compounds and their R_M values[21]. Jursik[22] determined the R_F values of some aminocarboxylatonickel(II) complexes by means of thin-layer chromatography on silica gel, using phenol–water (75:25) as the solvent system. He established that an increasing number of carbon atoms in a homologous series of coordinated amino acids results in an increase in the R_F values of the complexes. With regard to these results we wanted to establish (a) whether they represent part of a general regularity of the correlation between R_F values of metal complexes and the number of carbon atoms in coordinated

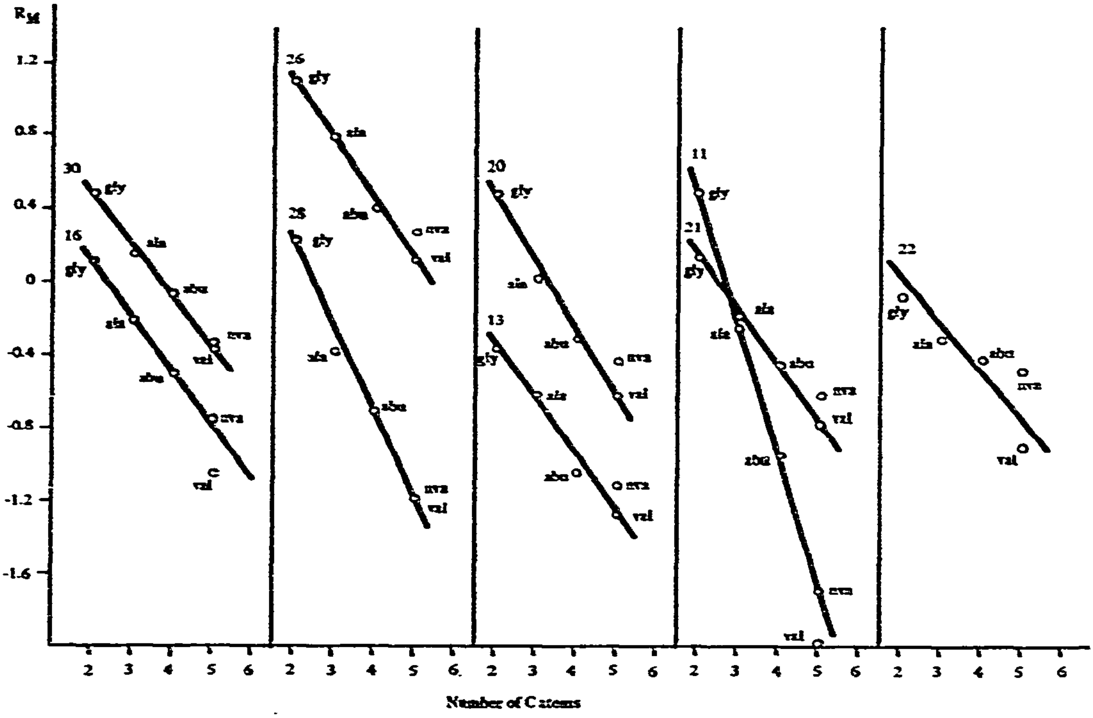
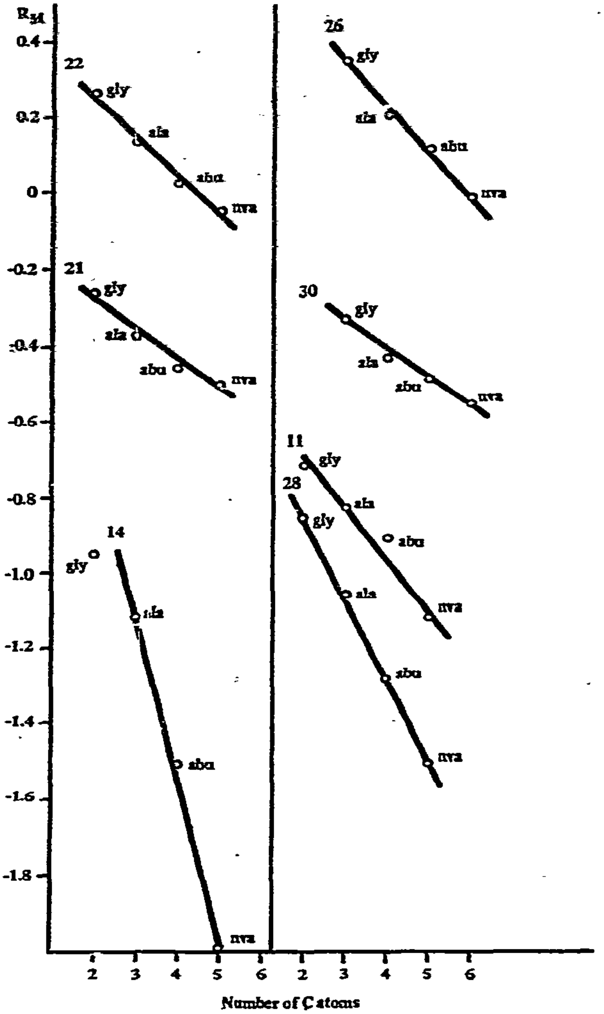


Fig. 3. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the $(+)_{589}$-*cis*(O),*trans*(NH_2)-[$CoNH_3Am_2NO_2$] complex. The numbers on the lines refer to the solvent systems used (see Table II).

amino acids, and (b) whether there is a linear correlation between the number of carbon atoms in aminocarboxylato ligands coordinated to cobalt(III) and the R_M values of the corresponding complexes. Therefore, we chromatographed 24 anionic and neutral aminocarboxylatocobalt(III) complexes (Table VII), divided into five homologous series, by means of ten two- and three-component solvent systems, all compounds of each type being separated by the use of at least five different solvent systems.



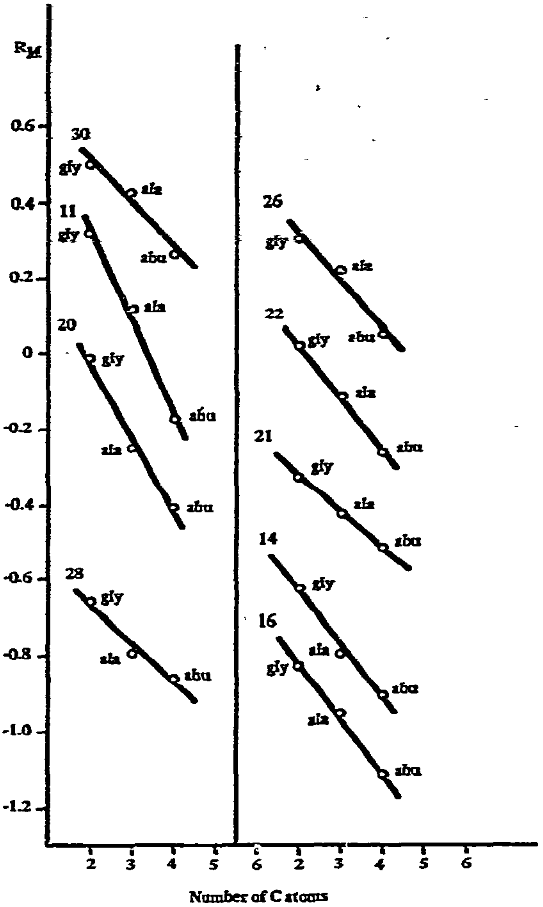


Fig. 4. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the $(-)_{589}$-meridional-$[CoNH_3Am(NO_2)_3]^-$ complex. The numbers on the lines refer to the solvent systems used (see Table II).

Fig. 5. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the $(+)_{589}$-*cis*(NO_2),*trans*(NH_2, NH_3)-$[Co(NH_3)_2Am(NO_2)_2]$ complex. The numbers on the lines refer to the solvent systems used (see Table II).

In these experiments it was established that an increasing number of carbon atoms in the branched chain of coordinated amino acids causes an increase in the R_F values of the complexes investigated. The increase takes place regardless of whether the carbon atoms belong to a straight or a branched chain of coordinated chelate ligands. The differences in the R_F values of complexes containing straight and branched chains with the same number of carbon atoms were small (Table VII).

In addition, we found a linear correlation between the number of carbon atoms in coordinated aminocarboxylato ligands and the R_M value of the complex (Figs. 2–6); the correlation was always negative.

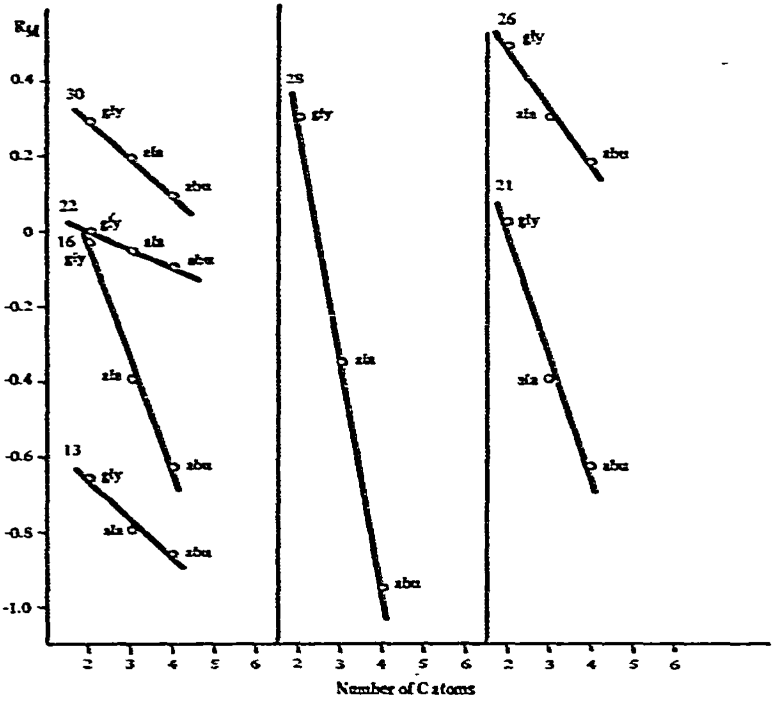


Fig. 6. Dependence of R_M value on the number of carbon atoms in one of the coordinated amino acids in the *trans*(NO_2),*cis*(NH_3)-$[Co(NH_3)Am(NO_2)_2]$ complex. The numbers on the lines refer to the solvent systems used (see Table II).

We assume that all of the above separations of complexes are achieved by a partition mechanism, as the CH_2 group is known to possess a very small adsorption energy[26], so that the separation could not be effected by an adsorption mechanism. Likewise, ion exchange cannot be taken as the cause of the separation, as the investigated complexes were of anionic and neutral types, and silica gel behaves as a weakly acidic cationic exchanger. The fact that analogous results are obtained by partition paper chromatography supports the postulated mechanism[2].

ACKNOWLEDGEMENT

The authors are grateful to the Serbian Republic Research Fund for financial support.

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