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EFFECT OF THE ABSOLUTE CONFIGURATION OF COBALT(III) COMPLEXES ON THEIR CHROMATOGRAPHIC BEHAVIOUR*

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SUMMARY

Seventeen pairs of diastereomeric cobalt(III) complexes were subject to paper chromatography using ten multi-component solvent systems, and nineteen diastereomeric pairs were chromatographed on silica gel G and aluminium oxide G thin layers by the use of sixteen single-component and fourteen multi-component solvent systems. It was established that in the paper chromatographic separations of complexes containing coordinated L-amino acids the diastereomers having Λ absolute configurations exhibited higher R_F values than those with Δ absolute configurations, in all the five homologous series studied, regardless of the solvent system used. However, in the thin-layer chromatographic separations on silica gel G and aluminium oxide G, respectively, the diastereomers having the same absolute configuration and containing coordinated amino acids of the same configuration always exhibited higher (or lower) R_F values only if they belonged to the same homologous series.

INTRODUCTION

As a continuation of earlier investigations on the effect of the composition and structure of cobalt(III) complexes on their chromatographic properties[4-6], we have studied the effect of the absolute configuration of such complexes on their R_F values obtained by paper and thin-layer chromatography on silica gel G and aluminium oxide G. In addition, we have investigated the effect of the sorbent and the solvent system used on the separation mechanism. All the investigations were carried out with compounds described mainly for the first time by us.

EXPERIMENTAL

Preparation of the complexes

The complexes were prepared according to procedures described in the literature (Tables II, V–VIII).

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* The paper chromatographic results were presented in part at the *XVII International Conference on Coordination Chemistry*[1], and the thin-layer chromatographic results at the *XXIII and XXIV Serbian Chemical Society Meetings*[2,3]

Paper chromatography

Paper chromatography was carried out in a cylinder (50 × 22 cm) by the ascending method on Whatman No. 1 paper strips (30 × 3 cm). The solvent was placed in the cylinder 1 h before the chromatographic separation, and travelled about 20 cm. The detection of the separated components was performed by dipping the developed paper strips into ammonium sulphide solution. All experiments were carried out at 22 ± 2°C. The solvent systems used are given in Table I, and the corresponding R_F values in Table II.

Thin-layer chromatography (TLC)

Chromatographic separations were performed by the ascending technique on silica gel G-MN (Laphoma, Skoplje, Yugoslavia) which contained 5% calcium sulphate, and in aluminium oxide G (Type 60/E) (E Merck, Darmstadt, G F.R.) which contained 10% calcium sulphate. A suspension of 30 g silica gel in 70 cm³ water, and 100 g of aluminium oxide in 100 cm³ of water, respectively, was applied on five and eight glass plates (19.5 × 13 × 0.5 cm), respectively, which had first been washed 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 or aluminium oxide 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 in the case of silica gel, and 30 min in case of aluminium oxide. 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 glass vessels (13.5 × 19.5 × 23.5 cm). One hour before the development the solvent was placed in a cylinder in order to saturate it with solvent vapour. The solvent systems consisting of p a. grade solvents, their compositions being listed in Tables III and IV. The solvent systems travelled about 10 cm and detection was performed by spraying the plates with an ammonium sulphide solution (2 mol/dm³). All investigations were performed at 20 ± 2°C.

TABLE I

SOLVENT SYSTEMS USED FOR PAPER CHROMATOGRAPHY

No.	Composition	Proportions (v/v/v)	Time of development (h)
1	Isopropanol–water–conc.HNO₃	75:20:5	14
2	Ethyl acetate–ethanol–water	50.30.20	5 5
3	Ethyl acetate–ethanol–water	60-25-15	6
4	Acetone–water–conc. HNO₃	75-20:5	6
5	Phenol saturated with 2 *M* HCl		12
6	Dioxan–water–KI	85:15:1 g per 100 cm³	6
7	Ethyl acetate–ethanol–water	70:20.10	6
8	*n*-Butanol saturated with 1 *M* HCl		12
9	Ethanol–water–conc. HNO₃	80:15.5	5
10	*n*-Butanol–ethanol–water	70:20 10	12

TABLE II

EFFECT OF THE ABSOLUTE CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR $R_f \times 100$ VALUES OBTAINED BY PAPER CHROMATOGRAPHY

No	Absolute config	Complex*	Ref	Solvent**									
				1	2	3	4	5	6	7	8	9	10
cis-NO₂ *trans* N													
1	Δ-(−)	[Co(L-ala)₂(NO₂)₂]⁻	7	75	85	–	91	30	–	18	–	–	6
2	Λ-(+)	[Co(L-ala)₂(NO₂)₂]⁻	7	87	95	–	95	35	–	21	–	–	9
3	Δ-(−)	[Co(D-ala)₂(NO₂)₂]⁻	7	–	–	–	–	36	–	25	–	–	10
4	Λ-(+)	[Co(D-ala)₂(NO₂)₂]⁻	7	–	–	–	–	32	–	19	–	–	7
5	Δ-(−)	[Co(L-abu)₂(NO₂)₂]⁻	8	–	–	–	–	50	–	38	–	–	28
6	Λ-(+)	[Co(L-abu)₂(NO₂)₂]⁻	8	–	–	–	–	58	–	45	–	–	31
7	Δ-(−)	[Co(L-nva)₂(NO₂)₂]⁻	8	–	–	–	–	65	–	63	–	–	56
8	Λ-(+)	[Co(L-nva)₂(NO₂)₂]⁻	8	–	–	–	–	66	–	66	–	–	63
9	Δ-(−)	[Co(L-val)₂(NO₂)₂]⁻	8	–	–	–	–	62	–	46	–	–	56
10	Λ-(+)	[Co(L-val)₂(NO₂)₂]⁻	8	–	–	–	–	64	–	61	–	–	63
11	Δ-(−)	[Co(L-nle)₂(NO₂)₂]⁻	8	–	–	–	–	68	–	80	–	–	87
12	Λ-(+)	[Co(L-nle)₂(NO₂)₂]⁻	8	–	–	–	–	73	–	85	–	–	89
13	Δ-(−)	[Co(L-leu)₂(NO₂)₂]⁻	8	–	–	–	–	64	–	83	72	81	–
14	Λ-(+)	[Co(L-leu)₂(NO₂)₂]⁻	8	–	–	–	–	70	–	85	76	86	–
15	Δ-(−)	[Co(gly)(L-val)(NO₂)₂]⁻	9	–	–	–	–	51	–	70	22	–	–
16	Λ-(+)	[Co(gly)(L-val)(NO₂)₂]⁻	9	–	–	–	–	53	–	73	23	–	–
17	Δ-(−)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	–	–	–	–	53	–	71	33	–	–
18	Λ-(+)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	–	–	–	–	58	–	72	35	–	–

TABLE II (continued)

No.	Absolute config.	Complex*	Ref.	Solvent**									
				1	2	3	4	5	6	7	8	9	10
cis-O-*trans*-NH₂													
19	Δ-(−)	[Co(NH₃)(L-ala)₂(NO₂)]	10	43	−	36	−	−	60	−	−	−	−
20	Λ-(+)	[Co(NH₃)(L-ala)₂(NO₂)]	10	47	−	39	−	−	65	−	−	−	−
21	Δ-(−)	[Co(NH₃)(L-abu)₂(NO₂)]	10	67	−	74	−	−	80	−	−	−	−
22	Λ-(+)	[Co(NH₃)(L-abu)₂(NO₂)]	10	68	−	80	−	−	83	−	−	−	−
23	Δ-(−)	[Co(NH₃)(L-nva)₂(NO₂)]	10	88	−	93	−	−	92	−	−	−	−
24	Λ-(+)	[Co(NH₃)(L-nva)₂(NO₂)]	10	91	−	95	−	−	94	−	−	−	−
25	Δ-(−)	[Co(NH₃)(L-val)₂(NO₂)]	10	80	−	89	−	−	90	−	−	−	−
26	Λ-(+)	[Co(NH₃)(L-val)₂(NO₂)]	10	90	−	92	−	−	97	−	−	−	−
trans-O *cis*-N													
27	Δ-(−)	[Co(en)(L-ala)₂]⁺	11	51	−	−	34	−	−	−	−	50	−
28	Λ-(+)	[Co(en)(L-ala)₂]⁺	11	67	−	−	43	−	−	−	−	61	−
C₁-*cis*-O													
29	Δ-(−)	[Co(en)(L-ala)₂]⁺	11	64	−	−	73	−	−	−	−	56	−
30	Λ-(+)	[Co(en)(L-ala)₂]⁺	11	73	−	−	76	−	−	−	−	68	−
cis NO₂-*trans*-NH₂													
31	Δ-(−)	[Co(tn)(L-val)(NO₂)₂]	12	70	−	−	−	−	−	75	−	−	84
32	Λ-(+)	[Co(tn)(L-val)(NO₂)₂]	12	84	−	−	−	−	−	82	−	−	92
33	Δ-(−)	[Co(tn)(D-ala)(NO₂)₂]	12	65	−	−	91	−	−	57	−	−	62
34	Λ-(+)	[Co(tn)(D-ala)(NO₂)₂]	12	63	−	−	84	−	−	54	−	−	54

* Abbreviations: L-alaH = L-alanine, L-abuH = L-2 aminobutyric acid, L-nvaH = L-norvaline; L valH = L valine; L-nlcH = L norleucine; L-lcuH = L-leucine, D-alaH = D-alanine; glyH = glycine; en = 1,2-diaminoethane; tn = 1,3-diaminopropane

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

TABLE III

ONE-COMPONENT SOLVENT SYSTEMS USED FOR TLC

No	Composition	Time of developments (min)	
		Silica gel	Aluminium oxide
1	Water	15	—
2	Methanol	15	20
3	Ethanol	40	40
4	n-Propanol	70	50
5	Isopropanol	60	105
6	n-Butanol	65	60
7	Isobutanol	70	65
8	sec -Butanol	85	—
9	Allyl alcohol	65	—
10	Acetylacetone	60	45
11	N,N-Dimethylformamide	25	15
12	Acetic acid	—	40
13	Ethylene glycol monomethyl ether	55	55
14	Ethylene glycol monoethyl ether	—	60
15	1,2-Propanediol	—	16 h
16	1 3-Propanediol	—	9 h

RESULTS AND DISCUSSION

Paper chromatography

As seen from the Experimental, the investigation of the effect of the absolute configuration of cobalt(III) complexes on their R_F values was carried out by chroma-

TABLE IV

MULTI-COMPONENT SOLVENT SYSTEMS USED FOR TLC

No	Composition	Proportions (v/v)	Time of developments (min)	
			Silica gel	Aluminium oxide
17	Methanol–water	80 20	25	45
18	Methanol–water	95 5	—	50
19	Ethanol–water	75 25	30	—
20	Methanol–ethanol	50 50	35	45
21	Methanol–ethanol	30 70	—	35
22	Methanol–water–conc HNO₃	75 20 5	25	—
23	Dioxan–water	80..20	—	45
24	Dioxan–water–KI	85 15 1 g per 100 cm³	65	55
25	n-Butanol–ethanol–water	70 20 10	65	65
26	Acetone–water–KI	85.15 1 g per 100 cm³	30	20
27	Ethylene glycol monomethyl ether–water	90 10	—	50
28	Ethylene glycol monoethyl ether–water	90 10	—	110
29	Ethyl acetate–ethanol–water	70 15 15	55	—
30	Ethyl acetate–ethanol–water	50 30-20	45	—

TABLE V

EFFECT OF THE ABSOLUTE CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR R_F × 100 VALUES OBTAINED BY TLC ON SILICA GEL G WITH ONE-COMPONENT SOLVENT SYSTEMS

No.	Absolute config.	Complex*	Ref.	Solvent**												
				1	2	3	4	5	6	7	8	9	10	11	13
cis-NO₂-*trans*-N															
1	Δ-(−)	[Co(L-ala)$_2$(NO$_2$)$_2$]$^-$	7	-	-	-	-	4	4	-	-	15	3	-	-
2	Λ-(+)	[Co(L-ala)$_2$(NO$_2$)$_2$]$^-$	7	-	-	-	-	6	7	-	-	18	5	-	-
3	Δ-(−)	[Co(L-abu)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	-	3	6	-	-	22	15	-	-
4	Λ-(+)	[Co(L-abu)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	-	6	11	-	-	34	20	-	-
5	Δ-(−)	[Co(L-nva)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	66	-	-	-	-	52	32	-	-
6	Λ-(+)	[Co(L-nva)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	69	-	-	-	-	56	34	-	-
7	Δ-(−)	[Co(L-val)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	-	-	14	5	-	-	38	-	-
8	Λ-(+)	[Co(L-val)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	-	-	19	8	-	-	47	-	-
9	Δ-(−)	[Co(L-nle)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	-	16	14	7	-	-	33	-	-
10	Λ-(+)	[Co(L-nle)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	-	20	30	11	-	-	36	-	-
11	Λ-(+)	[Co(L-leu)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	77	16	43	10	-	-	44	-	-
12	Δ-(−)	[Co(L-leu)$_2$(NO$_2$)$_2$]$^-$	8	-	-	-	82	18	46	13	-	-	46	-	-
13	Λ-(+)	[Co(D-ala)$_2$(NO$_2$)$_2$]$^-$	7	-	93	17	-	7	-	-	-	-	-	-	55
14	Δ-(−)	[Co(D-ala)$_2$(NO$_2$)$_2$]$^-$	7	-	90	12	-	3	-	-	-	-	-	-	46
15	Δ-(−)	[Co(gly)(L-val)(NO$_2$)$_2$]$^-$	9	-	73	-	-	-	-	5	-	-	3	-	-
16	Λ-(+)	[Co(gly)(L-val)(NO$_2$)$_2$]$^-$	9	-	76	-	-	-	35	7	-	-	6	-	-
17	Δ-(−)	[Co(gly)(L-leu)(NO$_2$)$_2$]$^-$	9	-	-	-	-	8	35	13	-	-	-	-	-
18	Λ-(+)	[Co(gly)(L-leu)(NO$_2$)$_2$]$^-$	9	-	-	-	-	12	43	16	-	-	-	-	-

cis O-trans-NH₂

Config	No.	Complex												
Δ(−)	19	[Co(NH₃)(L-ala)₂(NO₂)]	10	92	63	11	−	3	−	−	−	11	−	−	66
Λ-(+)	20	[Co(NH₃)(L-ala)₂(NO₂)]	10	94	70	20	−	5	−	−	−	16	−	−	70
Δ(−)	21	[Co(NH₃)(L-abu)₂(NO₂)]	10	−	81	−	−	18	−	−	−	37	−	−	−
Λ(+)	22	[Co(NH₃)(L-abu)₂(NO₂)]	10	−	85	−	−	21	−	−	−	40	−	−	−
Δ(−)	23	[Co(NH₃)(L-nva)₂(NO₂)]	10	83	90	−	13	24	32	−	−	−	−	−	−
Λ(+)	24	[Co(NH₃)(L-nva)₂(NO₂)]	10	85	93	−	22	28	35	−	−	−	−	−	−
Δ(−)	25	[Co(NH₃)(L-val)₂(NO₂)]	10	90	−	−	−	19	27	10	6	−	−	−	−
Λ(+)	26	[Co(NH₃)(L-val)₂(NO₂)]	10	93	−	−	−	22	32	13	9	−	−	−	−

trans-O cis-N

Config	No.	Complex												
Δ(−)	27	[Co(en)(L-ala)₂]⁺	11	47	7	−	−	−	−	−	−	−	−	−	−
Λ(+)	28	[Co(en)(L-ala)₂]⁺	11	42	4	−	−	−	−	−	−	−	−	−	−

C₁ cis O

Config	No.	Complex												
Δ(−)	29	[Co(en)(L-ala)₂]⁺	11	26	−	−	−	−	−	−	−	−	−	−	−
Λ(+)	30	[Co(en)(L-ala)₂]⁺	11	22	−	−	−	−	−	−	−	−	−	−	−

cis O-trans NH₂

Config	No.	Complex												
Δ(−)	31	[Co(tn)(L-val)(NO₂)₂]	12	−	74	−	43	−	14	9	10	52	−	−	−
Λ(+)	32	[Co(tn)(L-val)₂(NO₂)₂]	12	−	70	−	30	−	11	6	8	41	−	−	−
Δ(−)	33	[Co(tn)(D-ala)(NO₂)₂]	12	76	61	−	15	13	−	−	−	30	−	−	−
Λ(+)	34	[Co(tn)(D-ala)(NO₂)₂]	12	80	66	−	20	16	−	−	−	35	−	−	−

Meridional (1,2,6-)

Config	No.	Complex												
Δ(−)	35	[Co(L-ala)₃]	13	−	61	15	−	−	−	−	−	−	−	82	59
Λ(+)	36	[Co(L-ala)₃]	13	−	64	19	−	−	−	−	−	−	−	88	62
Δ(−)	37	[Co(L-val)₃]	14	−	85	74	−	41	26	13	8	−	−	88	87
Λ(+)	38	[Co(L-val)₃]	14	−	88	80	−	53	31	17	14	−	−	92	91

* Abbreviations as in Table II

** The compositions of the solvent systems are given in Table III

TABLE VI

EFFECT OF THE ABSOLUTE CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR $R_f \times 100$ VALUES OBTAINED BY TLC ON SILICA GEL G WITH MULTI-COMPONENT SOLVENT SYSTEMS

No.	Absolute config	Complex*	Ref	Solvent**								
				17	19	20	22	24	25	26	29	30
cis NO₂-*trans* N												
1	Δ-(−)	[Co(L-ala)₂(NO₂)₂]⁻	7	−	−	71	−	−	28	−	−	45
2	Λ-(+)	[Co(L-ala)₂(NO₂)₂]⁻	7	−	−	74	−	−	34	−	−	51
3	Δ-(−)	[Co(L-abu)₂(NO₂)₂]⁻	8	−	−	77	−	−	34	83	−	68
4	Λ-(+)	[Co(L-abu)₂(NO₂)₂]⁻	8	−	−	79	−	−	40	86	−	71
5	Δ-(−)	[Co(L-nva)₂(NO₂)₂]⁻	8	−	−	79	−	−	49	88	−	−
6	Λ-(+)	[Co(L-nva)₂(NO₂)₂]⁻	8	−	−	82	−	−	52	92	−	−
7	Δ-(−)	[Co(L-val)₂(NO₂)₂]⁻	8	−	−	77	−	−	46	86	−	−
8	Λ-(+)	[Co(L-val)₂(NO₂)₂]⁻	8	−	−	81	−	−	49	89	−	−
9	Δ-(−)	[Co(L-nle)₂(NO₂)₂]⁻	8	−	−	83	−	−	57	93	19	−
10	Λ-(+)	[Co(L-nle)₂(NO₂)₂]⁻	8	−	−	87	−	−	63	96	23	−
11	Δ-(−)	[Co(L-leu)₂(NO₂)₂]⁻	8	−	−	85	−	−	57	−	21	81
12	Λ-(+)	[Co(L-leu)₂(NO₂)₂]⁻	8	−	−	89	−	−	61	−	24	83
13	Δ-(−)	[Co(D-aln)₂(NO₂)₂]⁻	7	−	86	−	−	−	−	89	6	−
14	Λ-(+)	[Co(D ala)₂(NO₂)₂]⁻	7	−	80	−	−	−	−	84	3	−
15	Δ-(−)	[Co(gly)(L-val)(NO₂)₂]⁻	9	−	−	61	−	−	29	−	−	75
16	Λ-(+)	[Co(gly)(L-val)(NO₂)₂]⁻	9	−	−	65	−	−	34	−	−	79
17	Δ-(−)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	−	−	−	−	−	39	−	21	71
18	Λ-(+)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	−	−	−	−	−	44	−	24	74

	No.	Config	Complex									
cis-O-trans-NH₂												
	19	Δ-(−)	[Co(NH₃)(L-ala)₂(NO₂)]	74	76	37	—	46	28	70	6	36
	20	Λ-(+)	[Co(NH₃)(L-ala)₂(NO₂)]	77	79	44	—	53	36	76	9	44
	21	Δ-(−)	[Co(NH₃)(L-abu)₂(NO₂)]	—	74	61	—	58	44	85	14	56
	22	Λ-(+)	[Co(NH₃)(L-abu)₂(NO₂)]	—	76	74	—	61	49	87	18	61
	23	Δ-(−)	[Co(NH₃)(L-nva)₂(NO₂)]	—	83	82	—	—	65	—	38	—
	24	Λ-(+)	[Co(NH₃)(L-nva)₂(NO₂)]	—	86	85	—	—	70	—	42	—
	25	Δ-(−)	[Co(NH₃)(L-val)₂(NO₂)]	—	82	78	—	—	56	—	—	75
	26	Λ-(+)	[Co(NH₃)(L-val)₂(NO₂)]	—	85	81	—	—	62	—	—	78
trans-O cis-N												
	27	Δ-(−)	[Co(en)(L-ala)₂]⁺	9	6	—	80	28	—	44	—	—
	28	Λ-(+)	[Co(en)(L-ala)₂]⁺	6	3	—	77	25	—	38	—	—
C₁-cis O												
	29	Δ-(−)	[Co(en)(L-ala)₂]⁺	—	—	—	74	16	—	16	—	—
	30	Λ-(+)	[Co(en)(L-ala)₂]⁺	—	—	—	62	11	—	9	—	—
cis O trans-NH₂												
	31	Δ(−)	[Co(tn)(L-val)(NO₂)₂]	—	—	—	84	76	—	—	—	71
	32	Λ(↑)	[Co(tn)(L-val)(NO₂)₂]	—	—	51	81	64	—	—	—	68
	33	Δ(−)	[Co(tn)(D-ala)(NO₂)₂]	—	75	51	80	60	—	—	—	—
	34	Λ(+)	[Co(tn)(D-ala)(NO₂)₂]	—	78	67	89	63	—	—	—	—
Meridional (1,2,6-)												
	35	Δ(−)	[Co(L-ala)₃]	—	67	44	—	—	—	53	—	—
	36	Λ(+)	[Co(L-ala)₃]	—	70	47	—	—	—	57	—	—
	37	Δ(−)	[Co(L-val)₃]	—	85	84	—	—	—	89	27	—
	38	Λ(+)	[Co(L-val)₃]	—	88	87	—	—	—	92	36	—

* Abbreviations as in Table II

** The compositions of the solvent systems are given in Table IV

TABLE VII

EFFECT OF THE ABSOLUTE CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR R_f × 100 VALUES OBTAINED BY TLC ON ALUMINIUM OXIDE WITH ONE COMPONENT SOLVENT SYSTEMS

No.	Absolute config	Complex*	Ref	Solvent**												
				2	3	4	5	6	7	10	11	12	13	14	15	16
t(x-NO₂)-trans-N																
1	Δ-(−)	[Co(L-ala)₂(NO₂)₂]⁻	7	69	−	−	−	−	−	−	−	−	83	−	88	−
2	Λ-(+)	[Co(L-ala)₂(NO₂)₂]⁻	7	71	−	−	−	−	−	−	−	−	88	−	90	−
3	Δ-(−)	[Co(L-abu)₂(NO₂)₂]⁻	8	80	−	−	−	−	−	4	−	−	88	−	87	−
4	Λ-(+)	[Co(L-abu)₂(NO₂)₂]⁻	8	83	30	−	−	−	−	6	−	−	91	−	89	−
5	Δ-(−)	[Co(L-nva)₂(NO₂)₂]⁻	8	77	33	−	−	−	−	6	−	−	88	−	86	86
6	Λ-(+)	[Co(L-nva)₂(NO₂)₂]⁻	8	81	34	−	−	−	−	9	−	−	91	−	90	92
7	Δ-(−)	[Co(L-val)₂(NO₂)₂]⁻	8	77	36	−	4	11	11	6	−	−	87	−	86	−
8	Λ-(+)	[Co(L-val)₂(NO₂)₂]⁻	8	79	46	−	7	15	17	8	−	−	89	−	89	−
9	Δ-(−)	[Co(L-nle)₂(NO₂)₂]⁻	8	87	48	−	−	18	21	10	−	−	88	−	87	−
10	Λ-(+)	[Co(L-nle)₂(NO₂)₂]⁻	8	90	52	−	−	20	24	13	−	−	92	−	89	−
11	Δ-(−)	[Co(L-leu)₂(NO₂)₂]⁻	8	−	53	−	−	20	−	−	−	−	91	−	90	−
12	Λ-(+)	[Co(L-leu)₂(NO₂)₂]⁻	8	−	57	−	−	24	−	−	−	−	93	−	93	−
13	Δ-(−)	[Co(D-ala)₂(NO₂)₂]⁻	7	80	−	−	−	−	−	−	−	−	80	−	−	88
14	Λ-(+)	[Co(D-ala)₂(NO₂)₂]⁻	7	75	−	−	−	−	−	−	−	−	76	−	−	83
15	Δ-(−)	[Co(gly)(L-val)(NO₂)₂]⁻	9	70	−	−	−	4	−	−	−	−	81	−	−	84
16	Λ-(+)	[Co(gly)(L-val)(NO₂)₂]⁻	9	73	−	−	−	7	−	−	−	−	85	−	−	87
17	Δ-(−)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	48	−	−	−	−	−	−	−	−	86	−	−	85
18	Λ-(+)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	53	−	−	−	−	−	−	−	−	88	−	−	87

cis-O trans-NH₂

No.	Config	Complex												
19	Λ(−)	[Co(NH₃)(L-ala)₂(NO₂)]	10				5				84		6	90
20	Λ(+)	[Co(NH₃)(L-ala)₂(NO₂)]	10				7				86		9	94
21	Λ(−)	[Co(NH₃)(L-abu)₂(NO₂)]	10	66	10	8	10		6		84	91		
22	Λ(+)	[Co(NH₃)(L-abu)₂(NO₂)]	10	76	13	18	13		9		90	95		
23	Λ(−)	[Co(NH₃)(L-nva)₂(NO₂)]	10	75	37	35			12		82	93		
24	Λ(+)	[Co(NH₃)(L-nva)₂(NO₂)]	10	80	42	40			15		85	98		
25	Λ(−)	[Co(NH₃)(L-val)₂(NO₂)]	10	73	30	47	2				80			
26	Λ(+)	[Co(NH₃)(L-val)₂(NO₂)]	10	82	49	51	4				83			

trans-O cis-N

27	Δ-(−)	[Co(en)(L-ala)₂]⁺	11								83			
28	Δ-(+)	[Co(en)(L-ala)₂]⁺	11								79			

C₁-cis-O*

29	Δ-(−)	[Co(en)(L-ala)₂]⁺	11											
30	Δ-(+)	[Co(en)(L-ala)₂]⁺	11											

cis-O trans-NH₂

31	Δ-(−)	[Co(tn)(L-val)(NO₂)₂]	12	85	83	60	49		81	91	81			
32	Δ-(+)	[Co(tn)(L-val)(NO₂)₂]	12	83	76	51	42		73	91	70			
33	Δ-(−)	[Co(tn)(D-ala)(NO₂)₂]	12	81	60	31	4	45	39	79		93		
34	Δ-(+)	[Co(tn)(D-ala)(NO₂)₂]	12	83	63	38	8	49	45	90		97		

Meridional (1,2,6-)

35	Δ-(−)	[Co(L-ala)₃]	13	8	15								7	
36	Δ-(+)	[Co(L-ala)₃]	13	11	17								10	
37	Δ-(−)	[Co(L-val)₃]	14		87	44			31		77		95	
38	Λ(+)	[Co(L-val)₃]	14		90	47			37		87		98	

TABLE VIII

EFFECT OF THE ABSOLUTE CONFIGURATION OF THE MIXED COBALT(III) COMPLEXES ON THEIR $R_f \times 100$ VALUES OBTAINED BY TLC ON ALUMINIUM OXIDE WITH MULTI-COMPONENT SOLVENT SYSTEMS

No.	Absolute config	Complex*	Ref.	Solvent**									
				17	18	20	21	23	24	25	26	27	28
cis NO₂-trans N													
1	Δ-(−)	[Co(L-ala)₂(NO₂)₂]⁻	7	88	–	13	21	63	78	29	–	–	–
2	Δ-(+)	[Co(L-ala)₂(NO₂)₂]⁻	7	91	–	16	24	65	82	32	–	–	–
3	Δ-(−)	[Co(L-abu)₂(NO₂)₂]⁻	8	92	78	32	42	68	–	51	92	–	91
4	Λ-(+)	[Co(L-abu)₂(NO₂)₂]⁻	8	94	81	36	46	73	90	54	95	–	95
5	Δ-(−)	[Co(L-nva)₂(NO₂)₂]⁻	8	–	78	64	49	74	93	56	–	–	91
6	Δ-(+)	[Co(L-nva)₂(NO₂)₂]⁻	8	–	83	73	55	79	–	62	–	–	95
7	Λ-(−)	[Co(L-val)₂(NO₂)₂]⁻	8	–	84	80	50	70	–	52	–	–	89
8	Λ-(+)	[Co(L-val)₂(NO₂)₂]⁻	8	–	87	82	54	72	93	56	–	–	92
9	Δ-(−)	[Co(L-nle)₂(NO₂)₂]⁻	8	–	–	81	54	75	95	57	–	–	–
10	Λ(+)	[Co(L-nle)₂(NO₂)₂]⁻	8	–	84	85	63	81	91	63	–	–	92
11	Δ-(−)	[Co(L-leu)₂(NO₂)₂]⁻	8	–	84	82	61	78	94	68	–	–	92
12	Λ-(+)	[Co(L-leu)₂(NO₂)₂]⁻	8	–	86	84	66	81	–	71	–	–	94
13	Δ(−)	[Co(D-ala)₂(NO₂)₂]⁻	7	–	–	–	–	68	–	29	–	–	89
14	Λ(+)	[Co(D-ala)₂(NO₂)₂]⁻	7	–	–	–	–	53	–	26	–	–	87
15	Δ(−)	[Co(gly)(L-val)(NO₂)₂]⁻	9	–	72	46	17	62	–	22	87	–	–
16	Λ(+)	[Co(gly)(L-val)(NO₂)₂]⁻	9	–	76	50	20	75	–	25	94	–	–
17	Δ-(−)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	–	70	25	–	–	–	22	90	–	–
18	Λ(+)	[Co(gly)(L-leu)(NO₂)₂]⁻	9	–	73	28	–	–	–	27	93	–	–

No.	Ref.	Config.	Complex											
cis-O-trans NH₂														
19	10	Δ-(−)	[Co(NH₃)(L-ala)₂(NO₂)]	79	—	—	—	—	—	73	16	—	46	—
20	10	Λ-(+)	[Co(NH₃)(L-ala)₂(NO₂)]	82	—	—	—	—	—	78	24	—	49	—
21	10	Δ-(−)	[Co(NH₃)(L-abu)₂(NO₂)]	92	—	—	—	—	—	86	40	—	70	87
22	10	Λ-(+)	[Co(NH₃)(L-abu)₂(NO₂)]	94	—	—	—	—	—	90	54	—	80	91
23	10	Δ-(−)	[Co(NH₃)(L-nva)₂(NO₂)]	93	—	—	—	—	—	91	63	—	86	91
24	10	Λ-(+)	[Co(NH₃)(L-nva)₂(NO₂)]	95	—	—	—	—	—	93	74	—	93	97
25	10	Δ-(−)	[Co(NH₃)(L-val)₂(NO₂)]	90	—	—	—	—	—	87	62	—	—	—
26	10	Λ-(+)	[Co(NH₃)(L-val)₂(NO₂)]	92	—	—	—	—	—	94	75	—	—	—
trans-O cis N														
27	11	Δ-(−)	[Co(en)(L-ala)₂]⁺	37	—	—	—	—	—	73	—	—	—	—
28	11	Λ-(+)	[Co(en)(L-ala)₂]⁺	32	—	—	—	—	—	71	—	—	—	—
C₁-cis O														
29	11	Δ-(−)	[Co(en)(L-ala)₂]⁺	15	—	—	—	92	95	37	—	48	—	—
30	11	Λ-(+)	[Co(en)(L-ala)₂]⁺	7	—	—	—	90	93	31	—	40	—	—
cis-O-trans NH₂														
31	12	Δ-(−)	[Co(tn)(L-val)(NO₂)₂]	—	—	92	87	—	—	—	82	—	96	—
32	12	Λ-(+)	[Co(tn)(L-val)(NO₂)₂]	—	—	90	84	—	—	—	76	—	93	—
33	12	Δ-(−)	[Co(tn)(D-ala)(NO₂)₂]	—	83	87	76	—	—	—	60	87	90	—
34	12	Δ-(+)	[Co(tn)(D-ala)(NO₂)₂]	—	86	90	80	—	—	—	67	91	92	—
Meridional (1,2,6)														
35	13	Λ-(−)	[Co(L-ala)₃]	66	—	—	—	—	—	40	20	—	44	67
36	13	Λ-(+)	[Co(L-ala)₃]	71	—	—	—	—	—	43	23	—	46	69
37	14	Δ-(−)	[Co(L-val)₃]	96	—	—	—	—	—	87	84	—	—	—
38	14	Λ-(+)	[Co(L-val)₃]	98	—	—	—	—	—	92	88	—	—	—

* Abbreviations as in Table II

** The compositions of the solvent systems are given in Table IV

tographing seventeen pairs of diastereoisomeric cobalt(III) complexes of anionic, cationic and neutral types by the use of ten multi-component solvent systems The complexes contained one or several of the following ligands: aminocarboxylato, nitro, ammonia, 1,2-diaminoethane and 1,3-diaminopropane On the basis of the obtained R_F values, shown in Table II, it was established that in complexes containing coordinated L-amino acids, the diastereomers having the Λ absolute configuration exhibited higher R_F values than those with the Δ absolute configuration in all the five homologous series studied, regardless of the solvent system applied However, complexes containing coordinated D-amino acids (only two pairs of such complexes were investigated) exhibited the opposite chromatographic behaviour.

TLC

Silica gel G. Chromatography was carried out with twelve single-component (Table III) and nine multi-component solvent systems (Table IV). On the basis of the results obtained (Tables V and VI) it can be concluded that in each homologous series the diastereomers having the same absolute complex configuration, having coordinated amino acids of the same configuration, always exhibited higher (or lower) R_F values than the corresponding diastereomers having the opposite absolute complex configuration, regardless of the composition of the solvent system used.

Aluminium oxide G. The same complexes were chromatographed on aluminium oxide G by the use of thirteen single-component (Table III) and ten multi-component solvent systems (Table IV). The results obtained are shown in Tables VII and VIII, respectively. It may be seen that the patterns observed on silica gel G are valid also for separations on aluminium oxide G.

Possible separation mechanisms

By comparing the chromatographic behaviour of the investigated diastereomers on paper with that on silica gel G and aluminium oxide G thin layers, respectively, it may be concluded that their behaviours are different in principle. In paper chromatography the patterns observed were independent of the homologous series studied, whereas this was not the case in TLC. On this basis it can be assumed that the separation mechanisms involved are different. In view of the fact that in the TLC separations the same pattern is observed with either single- or multi-component solvent systems, it is unlikely that in these cases the separation is achieved by a partition mechanism, by means of which the separation is effected in paper chromatography. Accordingly, the TLC separation mechanism may be either adsorption or ion exchange or both. However, since silica gel G is known to behave as a cation exchanger[15], and aluminium oxide G as an ampholyte[16], the analogous results obtained in separations of the anionic diastereomers on both thin layers cannot be explained by assuming an ion-exchange mechanism. Therefore, the prevailing separation mechanism in paper chromatographic procedure is partition, and in TLC it is most probably an adsorption process.

Finally, it follows that the methods described offer a possibility for the determination of the absolute configurations of metal complexes.

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