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PHENOL EFFECT IN PAPER CHROMATOGRAPHY OF METAL COMPLEXES

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SUMMARY

The R_F values of 78 cobalt(III) and platinum(II) complexes have been determined using solvent systems containing phenols. When the complexes were chromatographed with solvent systems containing mono- or polyhydric phenols, the *trans* isomers were found to exhibit higher R_F values than those of the *cis* isomers, *i.e.*, to display "the phenol effect". However, by gradually decreasing the phenol content of a solvent system the phenol effect was found to disappear; in the cases of solvent systems containing small amounts of phenol, the addition of an electrolyte, or increasing its concentration, has a similar influence. The R_F values of the cobalt(III) complexes increase when a five-membered ring is substituted by a six-membered one, and there is a linear relationship between the R_M values and the number of substituted rings. For homologous series of cobalt(III) complexes, the R_F values increase with increasing number of C atoms in the branched chain of the ligand and there is a linear relationship between the R_M values and the number of C atoms in the aminocarboxylato ligand. Finally, in the cases of four pairs of diastereomeric cobalt(III) complexes, containing L-aminocarboxylato ligands, the diastereomers having absolute configuration Δ exhibit higher R_F values than those of absolute configuration Λ .

INTRODUCTION

In earlier papers¹⁻⁵ we have established that in paper chromatographic separations of octahedral cobalt(III) and chromium(III) complexes, as well as of square-planar platinum(II) complexes, the *cis* isomers exhibit higher R_F values than the corresponding *trans* ones. However, when solvent systems containing phenol as the main component were used, this elution order was reversed. In addition, when mixed diamine and/or aminocarboxylato cobalt(III) complexes were chromatographed with non-phenolic solvent systems, the R_F values were higher when five-membered rings are substituted by six-membered rings⁴, and increased with increasing chain branching of aminocarboxylato ligands. A linear relationship between the R_M values and the number of substituted rings and the number of C atoms in the branched chain

of the aminocarboxylato ligand, respectively, was observed. It has been also found⁷ that for mixed cobalt(III) complexes containing L-aminocarboxylato ligands the diastereomers with absolute configuration Λ exhibit higher R_F values than those with absolute configuration Δ , when chromatographed with non-phenolic solvent systems.

Continuing these investigations, we have studied in more detail the afore-mentioned trends using solvent systems containing phenols, and considered the factors which might account for the reversal of the elution order of *cis* and *trans* isomers.

EXPERIMENTAL

Preparation of complexes

All the investigated complexes were prepared by known methods (Tables II–VII).

Chromatographic investigations

Chromatographic separations were carried out by the ascending method on Whatman No. 1 paper strips, as described in detail in our previous paper⁸. However, when the solvent mixture contained polyhydric phenols, the detection was carried out by dipping the paper strips into ammonium sulphide solution, and then washing them under running water until the brown colour had disappeared. The solvent systems used are given in Table I. In the experiment in which the *cis* and *trans* isomers of $[\text{CoCl}(\text{SCN})(\text{en})_2]^+$ ($\text{en} = 1,2\text{-diaminoethane}$) were spotted onto the chromatographic paper from an aqueous solution saturated with phenol, *i.e.*, containing about 8% phenol, the paper strips were first air-dried, then chromatographed with the non-phenolic solvent system 32 (Table I). The following R_F values were obtained: *cis*, 0.84; *trans*, 0.60. Two-dimensional chromatography of these isomers was carried out also on Whatman No. 1 paper strips (25×15 cm), according to the method of Williams and Kirby⁹. The development time was about 3 h. In the first dimension the phenolic solvent 3 (Table I) was used, and the obtained R_F values were 0.37 (*cis*) and 0.76 (*trans*). Phenol was then removed by means of a stream of hot air. In the second dimension, the non-phenolic solvent system 32 (Table I) was used, and the R_F values were: 0.85 (*cis*) and 0.60 (*trans*). Before chromatography in the second dimension, the *cis* and *trans* isomers of the same complex as well as cobalt(II) chloride ($R_F = 0.15$) were spotted.

Electronic absorption spectra

Electronic absorption spectra of the geometrical isomers of $[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$ were recorded on a Super Scan 3 spectrophotometer from aqueous solution and aqueous solutions saturated with phenol. Visible spectra were taken for $5.0 \cdot 10^{-3}$ M solutions and spectra in the near-UV region with $3.0 \cdot 10^{-4}$ M solutions. The following absorption maxima (nm) and the corresponding molar extinction coefficients, ϵ ($\text{m}^2 \text{mol}^{-1}$) were obtained: (a) in aqueous solutions, *cis*, $\lambda_1 = 324$ ($\log \epsilon_1 = 2.62$), $\lambda_2 = 438$ nm ($\log \epsilon_2 = 1.32$); *trans*, $\lambda_1 = 347$ ($\log \epsilon_1 = 2.54$), $\lambda_2 = 436$ nm ($\log \epsilon_2 = 1.31$); (b) in water saturated with phenol, *cis*, $\lambda_1 = 325$ ($\log \epsilon_1 = 2.69$), $\lambda_2 = 436$ nm ($\log \epsilon_2 = 1.34$); *trans*, $\lambda_1 = 348$ ($\log \epsilon_1 = 2.58$), $\lambda_2 = 434$ nm ($\log \epsilon_2 = 1.32$).

TABLE I
SOLVENT SYSTEMS USED

No.	Composition	Component ratio*	
1	Phenol saturated with water	—	
2	Phenol saturated with 2 M hydrochloric acid	—	
3	Phenol-ethanol-water-lithium chloride	40:35:10:1	(w/v/v/w)
4	4- <i>tert.</i> -Butylphenol-ethanol-water	35:50:15	(w/v/v)
5	2,4-Dichlorophenol-ethanol-water	30:50:20	(w/v/v)
6	Pyrocatechol-ethanol-water	10:80:10	(w/v/v)
7	Resorcinol-ethanol-water	10:80:10	(w/v/v)
8	Hydroquinone-ethanol-water	10:80:10	(w/v/v)
9	Phloroglucinol-ethanol-water	10:80:10	(w/v/v)
10	Pyrogallol-ethanol-water	10:80:10	(w/v/v)
11	Phenol-ethanol-water	10:80:10	(w/v/v)
12	Phenol-ethanol-water	20:70:10	(w/v/v)
13	Phenol-ethanol-water	10:70:20	(w/v/v)
14	Phenol-ethanol-water	5:70:25	(w/v/v)
15	Phenol-ethanol-2 M hydrochloric acid	20:70:10	(w/v/v)
16	Phenol-ethanol-2 M hydrochloric acid	10:70:20	(w/v/v)
17	Phenol-ethanol-2 M hydrochloric acid	5:70:25	(w/v/v)
18	Phenol-ethanol-water-lithium chloride	20:70:10:2.5	(w/v/v/w)
19	Phenol-ethanol-water-lithium chloride	10:70:20:5	(w/v/v/w)
20	Phenol-ethanol-water-lithium chloride	5:70:25:10	(w/v/v/w)
21	Phenol-ethanol-water-potassium iodide	10:70:20:5	(w/v/v/w)
22	Phenol-ethanol-water-potassium iodide	5:70:25:10	(w/v/v/w)
23	Phenol-ethanol-water	40:35:10	(w/v/v)
24	Phenol-ethanol-water	60:20:20	(w/v/v)
25	Phenol-ethanol-water	40:40:20	(w/v/v)
26	Phenol-ethanol-2 M hydrochloric acid	40:35:10	(w/v/v)
27	Phenol-ethanol-2 M hydrochloric acid	60:20:20	(w/v/v)
28	Phenol-ethanol-2 M hydrochloric acid	40:40:20	(w/v/v)
29	Cyclohexanol-ethanol-water	80:15:20	(v/v/v)
30	Anisole-ethanol-water	54:20:6	(v/v/v)
31	Benzyl alcohol-ethanol-water	60:25:15	(v/v/v)
32	Acetone-water-conc. nitric acid	75:20:5	(v/v/v)

* v refers to volume in ml, w to weight in g.

RESULTS

Effect of geometrical configuration on the R_F values of the complexes

As seen from Tables II and III, by chromatographing 30 platinum(II) and cobalt(III) complexes of cationic and neutral types with solvent systems containing phenols, the *trans* isomers exhibited higher R_F values than the corresponding *cis* ones ("the phenol effect"), except when the phenol content was only a few per cent (solvent system 14, Table II). This order was reversed for the isomers of $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$. However, as Table IV shows, the addition of an electrolyte to a chromatographic solvent containing a small phenol content resulted in the disappearance of the phenol effect in all cases.

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

The effect of the chelate ring size was investigated for seventeen cobalt(III)

TABLE II
EFFECT OF PHENOLS ON R_F VALUES OF *cis* AND *trans* ISOMERIC SQUARE-PLANAR COMPLEXES

No.	Isomer	Complex*	Ref.	$R_F \times 100^{**}$												
				1	2	3	4	5	11	12	13	14	29	30	31	
1	<i>cis</i>	[PtCl ₂ (NH ₃) ₂]	10	33	24	8	5	20	—	—	—	14	9	8	16	
2	<i>trans</i>		10	45	30	14	8	23	—	—	—	12	7	4	4	
3	<i>cis</i>	[PtBr ₂ (NH ₃) ₂]	11	38	30	20	9	—	17	—	21	29	18	16	—	
4	<i>trans</i>		11	46	40	27	13	—	19	—	24	25	16	9	—	
5	<i>cis</i>	[PtI ₂ (NH ₃) ₂]	11	42	34	32	20	—	33	—	38	53	58	41	—	
6	<i>trans</i>		11	53	50	43	25	—	35	—	41	49	54	31	—	
7	<i>cis</i>	[Pt(SCN) ₂ (NH ₃) ₂]	12	64	58	46	—	46	48	43	—	44	60	38	64	
8	<i>trans</i>		12	78	78	56	—	52	53	47	—	38	52	33	62	
9	<i>cis</i>	[Pt(SCN) ₂ (py) ₂]	12	94	—	96	—	95	—	—	—	—	98	—	—	
10	<i>trans</i>		12	96	—	98	—	97	—	—	—	—	96	—	—	
11	<i>cis</i>	[PtCl ₂ (py) ₂]	13	95	—	—	—	96	—	—	—	98	5	—	—	
12	<i>trans</i>		13	97	—	—	—	98	—	—	—	96	3	—	—	
13	<i>cis</i>	[Pt(NH ₃) ₂ (py) ₂] ²⁺	14	93	94	93	3	69	—	58	51	54	5	10	26	
14	<i>trans</i>		14	98	98	97	8	79	—	62	58	46	0	6	22	
15	<i>cis</i>	[Pt(NH ₃) ₂ (hx) ₂] ²⁺	15	14	6	2	5	—	—	8	—	—	—	4	—	
16	<i>trans</i>		15	18	8	4	9	—	—	10	—	—	—	2	—	

* py = Pyridine; hx = hydroxylamine.

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

complexes of cationic, anionic and neutral types (Table V) containing five- and/or six-membered aminocarboxylato and/or diamine chelate ligands, with nine phenolic solvent systems. In all the cases, enlargement of the chelate ring resulted in higher R_F values. A linear relationship between the corresponding R_M values and the number of substituted five-membered by six-membered rings has been established (Fig. 1).

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

Four homologous series of cobalt(III) complexes of anionic and neutral types were chromatographed with nine phenolic solvent systems (Table VI). An increase in the number of C atoms in the aminocarboxylato ligand was found to give rise to higher R_F values. In addition, a linear relationship between the R_M values and the number of C atoms in the aminocarboxylato ligand was established (Figs. 2 and 3).

Effect of absolute configuration on the R_F values of the complexes

As seen from Table VII, four pairs of diastereomeric cobalt(III) complexes containing L-aminocarboxylato ligands were investigated. It was found that the diastereomers having absolute configuration Λ exhibit higher R_F values than those having absolute configuration Δ .

Separations of geometrical isomers with solvent systems containing anisole, cyclohexanol or benzyl alcohol as the main component

As seen from Tables II and III, when chromatographing the investigated geometrical isomers with the solvent systems 29–31 (Table I), in all cases in which sep-

TABLE III
EFFECT OF PHENOLS ON R_F VALUES OF *cis* AND *trans* ISOMERIC OCTAHEDRAL COMPLEXES

No.	Isomer	Complex*	Ref.	$R_F \times 100^{**}$																																
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31		
1	<i>cis</i>	$[\text{CoCl}_2(\text{en})_2]^+$	18,19	-	95	40	16	43	38	38	-	33	49	26	30	53	51	4	24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	<i>trans</i>		18,19	-	98	69	31	66	56	66	-	52	58	38	52	68	60	2	15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	<i>cis</i>	$[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$	19	94	95	52	17	43	-	-	-	-	-	33	27	49	48	5	11	31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	<i>trans</i>		19	97	97	75	19	45	-	-	-	-	-	35	36	52	51	2	8	29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	<i>cis</i>	$[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$	20	95	94	45	18	44	-	63	-	59	-	25	35	54	54	38	-	28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	<i>trans</i>		20	98	97	54	22	49	-	68	-	62	-	32	40	60	61	28	-	19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	<i>cis</i>	$[\text{Co}(\text{SCN})_2(\text{en})_2]^+$	19,21	-	-	73	22	53	68	63	-	64	-	62	36	73	72	32	-	79	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	<i>trans</i>		19,21	-	-	82	34	66	72	72	-	69	-	66	63	76	74	29	-	75	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	<i>cis</i>	$[\text{Co}(\text{SCN})\text{Cl}(\text{en})_2]^+$	19,21	-	96	52	26	46	-	63	60	-	60	42	45	69	65	6	-	59	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
10	<i>trans</i>		19,21	-	98	82	35	62	-	65	63	-	64	52	62	74	72	4	-	52	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	<i>cis</i>	$[\text{Co}(\text{NO}_2)_2(\text{tn})_2]^+$	22	-	-	84	28	67	-	-	-	-	-	58	62	69	-	8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	<i>trans</i>		22	-	-	90	35	73	-	-	-	-	-	62	70	72	-	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
13	<i>cis</i>	$[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	18,23	43	25	5	25	-	-	-	-	-	-	12	9	-	-	4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
14	<i>trans</i>		18,23	39	21	3	21	-	-	-	-	-	-	9	-	-	-	4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* en = 1,2-Diaminoethane; tn = 1,3-diaminopropane.

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

TABLE IV
INFLUENCE OF ELECTROLYTE ON PHENOL EFFECT

No.	Isomer	Complex	Ref.	$R_F \times 100^*$																
				12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	<i>cis</i>	$[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$	20	27	49	48	21	27	42	38	53	58	51	52	53	75	51	68	52	46
2	<i>trans</i>		20	36	52	51	10	15	32	24	48	35	20	22	66	86	62	70	66	54
3	<i>cis</i>	$[\text{Co}(\text{SCN})_2(\text{en})_2]^+$	19,21	35	54	54	-	56	70	-	-	-	52	60	64	84	73	74	74	69
4	<i>trans</i>		19,21	40	60	61	-	42	58	-	-	-	37	38	82	96	80	82	82	81
5	<i>cis</i>	$[\text{Co}(\text{NO}_2)_2(\text{en})_2]^+$	19	36	73	62	17	25	42	36	52	54	45	50	54	68	50	62	51	45
6	<i>trans</i>		19	63	76	66	14	20	36	33	46	42	26	32	72	80	74	72	78	72

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

TABLE V
EFFECT OF PHENOLS ON R_f VALUES OF OCTAHEDRAL COMPLEXES CONTAINING FIVE- AND/OR SIX-MEMBERED CHELATE LIGANDS

No.	Isomer	Complex*	Ref.	$R_f \times 100^{**}$	1	2	3	4	5	11	12	13	14	29	30
1	<i>cis</i> -NO ₂ - <i>trans</i> -N	[Co(NO ₂) ₂ (gly) ₂] ⁻	16	46	37	18	18	3	5	9	15	31	40	2	—
2	<i>cis</i> -NO ₂ - <i>trans</i> -N	gly(β -ala)	17	66	52	28	28	6	9	17	24	39	44	5	—
3	<i>cis</i> -NO ₂ - <i>trans</i> -N	(β -ala) ₂	16	82	66	40	40	13	14	29	36	49	49	8	—
4	<i>cis</i> -O- <i>trans</i> -NH ₂	[Co(NO ₂) ₂ (gly) ₂ (NH ₃)]	24	56	—	10	10	2	6	6	—	—	52	3	—
5	<i>cis</i> -O- <i>trans</i> -NH ₂	(β -ala) ₂	24	98	—	70	70	18	21	20	—	—	68	6	—
6	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂ -NH ₃	[Co(NO ₂) ₂ (gly)(NH ₃) ₂]	24	51	—	13	13	2	11	9	—	—	55	5	7
7	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂ -NH ₃	(β -ala)	24	56	—	33	33	10	26	15	—	—	63	10	11
8	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Co(NO ₂) ₂ (gly)(en)]	25	35	—	11	11	2	4	25	—	—	69	2	2
9	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	(β -ala)	17	98	—	83	83	22	61	36	—	—	73	8	15
10	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Co(NO ₂) ₂ (gly)(tm)]	17	72	—	—	—	—	60	—	—	—	—	14	20
11	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	(β -ala)	17	98	—	—	—	—	96	—	—	—	—	18	28
12	<i>trans</i> -NO ₂	[Co(NO ₂) ₂ (en)] ⁺	20	86	83	53	53	13	53	25	37	47	49	5	—
13	<i>trans</i> -NO ₂	en(tm)	17	92	91	66	66	20	72	40	47	58	59	8	—
14	<i>trans</i> -NO ₂	(tm) ₂	22	97	96	78	78	28	91	53	55	69	66	10	—
15	Meridional (1,2,6)	[Co(gly) ₃]	26	50	47	9	9	2	6	7	9	20	27	2	—
16	Meridional (1,2,6)	(gly) ₂ (β -ala)	27	68	74	18	18	6	9	10	12	25	32	3	—
17	Meridional (1,2,6)	(β -ala) ₃	28	82	90	32	32	14	—	16	16	34	39	4	—

* glyH = Glycine; β -alaH = β -alanine.

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

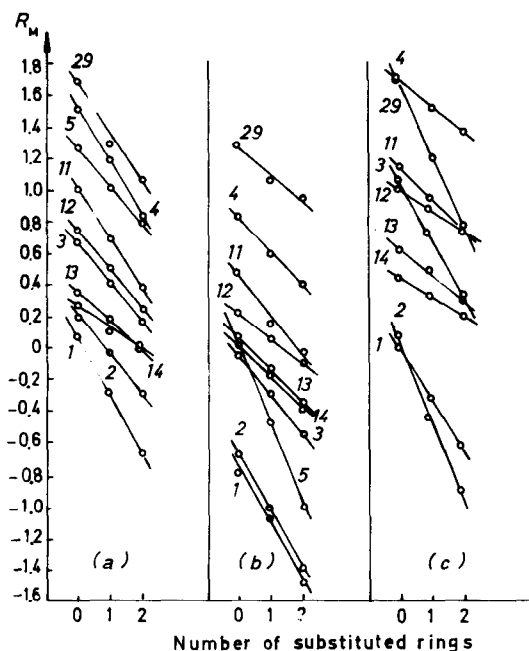


Fig. 1. Dependence of R_M values on the number of five-membered rings substituted by the corresponding six-membered rings in solvent systems containing phenol. Complexes: a, 1-3; b, 12-14; c, 15-17 (see Table V). The numbers on the lines refer to the solvent systems used (see Table I).

aration was achieved, the *cis* isomers were found to exhibit higher R_F values than those of the *trans* ones.

DISCUSSION

From our results it is seen that, of the four trends which had been established earlier by using non-phenolic solvent systems¹⁻⁷, a reversal of the elution order of isomeric complexes (R_F *trans* > R_F *cis*) was observed only when the *cis* and *trans* geometrical isomers were chromatographed with solvent systems containing phenols (the "phenol effect"). An exception was the isomeric $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$, which was rather surprising.

By using solvent systems containing anisole, cyclohexanol or benzyl alcohol instead of phenol, the *cis* isomers were found to exhibit higher R_F values than the corresponding *trans* ones. This indicates that the replacement of the hydrogen of the phenolic group by a methyl group, hydrogenation of the aromatic nucleus or displacement of the OH group from the aromatic nucleus to the side chain bring about the disappearance of the phenol effect.

The phenol effect could be due either to the interaction of phenol with the investigated isomers, or to the interaction of phenol with cellulose. From the following it can be concluded that phenol does not form compounds with the investigated complexes in the course of chromatography.

(a) When the *cis* and *trans* geometrical isomers were chromatographed with

TABLE VI
EFFECT OF PHENOLS ON R_f VALUES OF OCTAHEDRAL COMPLEXES CONTAINING DIFFERENT NUMBERS OF CARBON ATOMS IN THE BRANCHED CHAIN

No.	Isomer	Complex*	Ref.	$R_f \times 100^{**}$	1	2	3	4	5	11	12	13	14	29	30
1	<i>cis</i> -NO ₂ - <i>trans</i> -N	[Co(NO ₂) ₂ (gly) ₂] ⁻	29	39	20	22	22	3	3	18	13	37	46	2	-
2	(+) ^{***} - <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -ala) ₂	29	61	28	44	44	7	14	39	28	60	66	5	-
3	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -abu) ₂	30	80	49	65	65	16	50	67	45	76	80	11	-
4	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -bu) ₂	30	83	52	68	68	18	52	68	47	74	78	13	-
5	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -nva) ₂	30	88	65	85	85	36	66	76	70	80	86	34	-
6	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -nle) ₂	30	89	64	84	84	38	65	77	73	81	85	36	-
7	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -leu) ₂	30	94	73	94	94	62	91	87	80	89	92	80	-
8	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -leu) ₂	30	96	73	95	95	65	92	88	83	91	92	82	-
9	(+)- <i>cis</i> -NO ₂ - <i>trans</i> -N	(<i>t</i> -ile) ₂	30	95	75	98	98	66	93	89	82	92	93	82	-
10	<i>cis</i> -O- <i>trans</i> -NH ₂	[Co(NO ₂) ₂ (gly) ₂ (NH ₃)]	24	40	30	12	10	4	16	11	24	16	16	5	-
11	(+)- <i>cis</i> -O- <i>trans</i> -NH ₂	(<i>t</i> -ala) ₂	24	82	82	48	23	18	38	38	23	53	54	14	-
12	(+)- <i>cis</i> -O- <i>trans</i> -NH ₂	(<i>t</i> -abu) ₂	31	98	98	74	41	-	59	42	67	72	72	28	-
13	(+)- <i>cis</i> -O- <i>trans</i> -NH ₂	(<i>t</i> -nva) ₂	31	-	-	96	58	-	79	66	84	84	74	52	-
14	(+)- <i>cis</i> -O- <i>trans</i> -NH ₂	(<i>t</i> -val) ₂	31	-	-	97	60	-	80	68	83	94	94	53	-
15	Meridional (1,2,6)	[Co(NO ₂) ₃ (gly)(NH ₃)] ⁻	32	38	25	-	10	5	17	-	-	-	67	6	6
16	(-)-Meridional (1,2,6)	L-ala	32	43	31	-	16	7	32	-	-	-	72	8	8
17	(-)-Meridional (1,2,6)	L-abu	32	46	36	-	20	13	43	-	-	-	77	12	11
18	(-)-Meridional (1,2,6)	L-nva	32	58	50	-	28	18	54	-	-	-	83	15	15
19	(-)-Meridional (1,2,6)	L-val	32	56	48	-	28	17	51	-	-	-	84	16	15
20	(-)-Meridional (1,2,6)	L-leu	32	60	58	-	37	24	62	-	-	-	86	22	19
21	<i>trans</i> -NO ₂ - <i>cis</i> -NH ₃	[Co(NO ₂) ₂ (gly)(NH ₃) ₂]	24	44	29	13	4	6	10	10	10	23	28	5	-
22	<i>trans</i> -NO ₂ - <i>cis</i> -NH ₃	L-ala	24	61	42	23	8	11	21	21	18	33	39	8	-
23	<i>trans</i> -NO ₂ - <i>cis</i> -NH ₃	L-abu	24	69	52	32	13	21	21	27	28	46	50	12	-

* 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 I.

*** Sign of optical rotation at 589 nm.

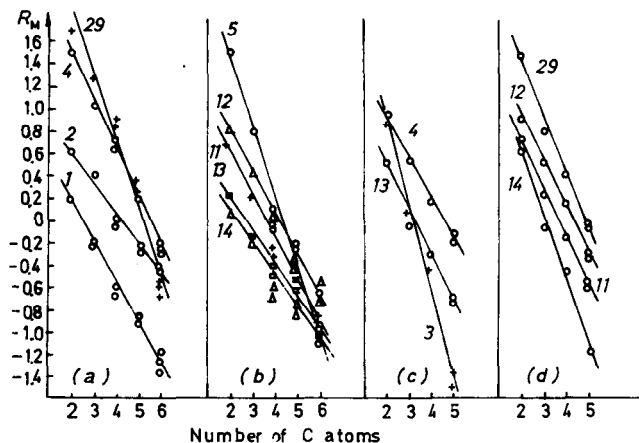


Fig. 2. Dependence of R_M values on the number of carbon atoms in one of the coordinated amino acids (Am) using solvent systems containing phenol. Complexes: a, b (+)₅₈₉-*cis*(NO₂),*trans*(N)-[Co(Am)₂(NO₂)₂]⁻; c, d *cis*(O),*trans*(NH₂)-[Co(Am)₂(NO₂)(NH₃)]. The numbers on the lines refer to the solvent systems used (see Table I).

the non-phenolic solvent system 32 (Table I) after being spotted from aqueous solutions saturated with phenol, the *cis* isomer exhibited the higher R_F value.

(b) Two-dimensional chromatography of the isomeric [CoCl(SCN)(en)₂]⁺ showed that the use of the phenolic solvent system 3 (Table I) in the first dimension resulted in a higher R_F value for the *trans* isomer. On removal of phenol from the paper, the use of the non-phenolic solvent system 32 (Table I) in the second dimension gave rise to a higher R_F value for the *cis* isomer.

(c) Elemental analysis of the isomeric [Co(NO₂)₂(en)₂]NO₃ recrystallized from

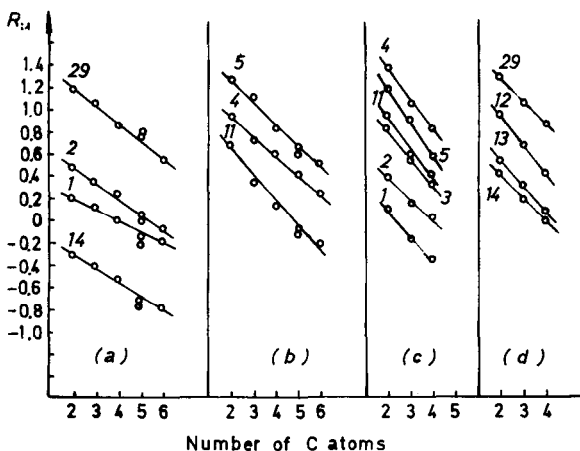


Fig. 3. Dependence of R_M values on the number of carbon atoms in one of the coordinated amino acids (Am) using solvent systems containing phenol. Complexes: a, b (-)₅₈₉-*mer*-[Co(Am)(NO₂)₃(NH₃)]⁻; c, d *trans*(NO₂),*cis*(NH₃)-[Co(Am)(NO₂)₂(NH₃)₂]. The numbers on the lines refer to the solvent systems used (see Table I).

TABLE VII

EFFECT OF PHENOLS ON R_F VALUES OF DIASTEREOMERIC OCTAHEDRAL COMPLEXES³⁰

No.	Absolute config.	Complex	$R_F \times 100^*$										
			1	2	3	4	5	11	12	13	14	29	30
<i>cis</i> -NO ₂ - <i>trans</i> -N													
1	$\Delta(-)$	[Co(NO ₂) ₂ (L-nva) ₂] ⁻	90	94	66	45	67	78	74	68	83	33	—
2	$\Delta(+)$	[Co(NO ₂) ₂ (L-nva) ₂] ⁻	92	96	70	48	72	80	76	72	86	37	—
3	$\Delta(-)$	[Co(NO ₂) ₂ (L-val) ₂] ⁻	93	64	91	44	—	—	75	70	90	34	—
4	$\Delta(+)$	[Co(NO ₂) ₂ (L-val) ₂] ⁻	95	66	93	50	—	—	77	74	93	38	—
5	$\Delta(-)$	[Co(NO ₂) ₂ (L-nleu) ₂] ⁻	—	68	—	—	82	86	76	90	—	66	—
6	$\Delta(+)$	[Co(NO ₂) ₂ (L-nleu) ₂] ⁻	—	73	—	—	85	88	79	92	—	68	—
7	$\Delta(-)$	[Co(NO ₂) ₂ (L-leu) ₂] ⁻	95	68	—	66	78	—	75	88	85	68	—
8	$\Delta(+)$	[Co(NO ₂) ₂ (L-leu) ₂] ⁻	98	71	—	69	81	—	77	90	88	70	—

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

water saturated with phenol showed that the products contained neither water nor phenol, and that the complexes underwent no chemical change.

(d) The absorption spectra of isomeric [Co(NO₂)₂(en)₂]NO₃ in water, and in water saturated with phenol, are very similar, indicating that no chemical reaction occurs between phenol and these complexes.

Accordingly, our results might be explained by the interaction of phenol with cellulose. In extensive investigations on the behaviour of solvent systems in paper chromatographic separations, Michal and Ackermann³³⁻³⁵ established that all the components of the solvent system take part in the formation of the stationary phase, and hence, in our case, phenol is involved as well. Horner *et al.*³⁶ found that, from aqueous solutions, phenol is preferentially fixed to cellulose. Similar results had been obtained earlier by Brass³⁷ in a study of the equilibria between cellulose and aqueous phenolic solutions; he established that phenol is partitioned between cellulose and water according to Henry's law. Therefore we have assumed that the phenol effect appears when the content of phenol in the stationary phase reaches a certain level. This is supported by the following facts:

(1) by gradually decreasing the phenol content of a solvent system the phenol effect was found to disappear, provided that the separation is possible

(2) for solvent systems containing small amounts of phenol, which are however sufficient to produce the phenol effect, the addition of an electrolyte, or increasing its concentration, also results in the disappearance of this effect.

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