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EFFECT OF THE COMPOSITION AND STRUCTURE OF COBALT(III) COMPLEXES ON THEIR R_F VALUES OBTAINED BY PARTITION PAPER CHROMATOGRAPHY

I. EFFECT OF THE POSITION OF NITRO GROUPS AND THE CHELATE RING SIZE

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SUMMARY

R_F values of 41 cobalt(III) complexes were determined by partition paper chromatography using 15 solvent systems. It was established that *cis*-NO₂ isomers always exhibit higher R_F values than the corresponding *trans*-isomers, even when a complex has several *cis*- and *trans*-isomers. It has been found that an increase in the chelate ring size gives rise to higher R_F values and that there is a linear dependence between the R_M values observed and the number of five-membered rings that are substituted by the corresponding six-membered rings.

INTRODUCTION

In earlier work, Stefanović and co-workers¹⁻³ carried out the paper chromatography of 12 pairs of geometrical isomers of cobalt(III), chromium(III) and platinum(II) complex compounds of the cationic type and established that the *cis*-isomers exhibit higher R_F values than the corresponding *trans*-isomers. In this work, we have extended this study to a larger number of nitro-cobalt(III) complexes of the anionic, cationic and neutral types, containing five-membered and six-membered diamino and/or aminocarboxylato chelate ligands. In addition, we have studied the effect of the chelate ring size on the R_F values of these complexes. These investigations were carried out predominantly with compounds recently prepared for the first time in our laboratory.

EXPERIMENTAL

Preparation of complexes investigated

All of the complexes used were prepared according to procedures described in the literature (Tables II and III).

Chromatographic investigation

Chromatography was carried out in a 50 × 22 cm cylinder 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. The solvent travelled about 22 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 room temperature. The solvent systems used are given in Table I.

TABLE I
SOLVENT SYSTEMS USED

No.	Composition	Component ratio*	Development time (h)
1	Isopropanol-water-conc. HNO ₃	75:20:5 (v/v/v)	14
2	Ethyl acetate-ethanol-water	50:30:20 (v/v/v)	5.5
3	Ethyl acetate-ethanol-water	60:25:15 (v/v/v)	6
4	Acetone-water-conc. HNO ₃	75:20:5 (v/v/v)	6
5	Phenol saturated with 2 N HCl		12
6	Dioxan-water-KI	85:15:1 (v/v/w)	6
7	Acetone-water-acetic acid	85:10:5 (v/v/v)	6
8	Dioxan-water-KI	75:25:1 (v/v/w)	5.5
9	Ethanol-water-conc. HNO ₃	80:15:5 (v/v/v)	5
10	Ethanol-water	80:20 (v/v)	5
11	Dioxan-water	80:20 (v/v)	6
12	Methanol-water-conc. HNO ₃	90:5:5 (v/v/v)	4

* v refers to volume in millilitres; w refers to weight in grams.

RESULTS AND DISCUSSION

Effect of the geometrical configuration on the R_F values of the complexes investigated

As seen from Table II, the effect of the geometrical configuration was studied on 18 cobalt(III) complexes containing some of the following six ligands: nitro groups, glycine (glyH), β -alanine (β -alaH), ammonia, ethylenediamine (en) or 1,3-trimethylenediamine* (tn). Most of these complexes are aminocarboxylato complexes, the chromatographic behaviour of which has not previously been investigated. The chromatography was carried out with seven solvent systems which contained, in addition to water, some of the following six organic solvents: ethanol, isopropanol, ethyl acetate, acetone, dioxan or phenol. Except in one instance, the solvent systems contained various amounts of some of the following electrolytes: potassium iodide, nitric acid, hydrochloric acid or acetic acid. On the basis of the R_F values obtained, it can be concluded that the *cis*-isomers always exhibit higher R_F values than the corresponding *trans*-isomers, which is consistent with the results of Stefanović and co-workers¹⁻³. In addition, as can be seen from the R_F values obtained for four geometric isomers of the dinitro diglycinatocobaltate(III) ion, both *cis*-NO₂ isomers exhibit higher R_F -values than each *trans*-NO₂ isomer. On this basis, it might be concluded that in these complexes the nitro groups are mainly responsible for the order of R_F values, although

* 1,3-Diaminopropane.

TABLE II
EFFECT OF THE POSITION OF THE NITRO GROUPS ON THE R_F VALUES

No.	Isomer	Complex	Ref.	$R_F \times 100^*$						
				1	2	3	4	5	6	7
1	<i>cis</i> -NO ₂ - <i>trans</i> -N	[Cogly ₂ (NO ₂) ₂] ⁻	4	68	44	—	76	—	—	—
2	<i>cis</i> - <i>cis</i> - <i>cis</i>	[Cogly ₂ (NO ₂) ₂] ⁻	4	53	39	—	65	—	—	—
3	<i>trans</i> -NO ₂ - <i>cis</i> -N	[Cogly ₂ (NO ₂) ₂] ⁻	4	31	16	—	54	—	—	—
4	<i>trans</i> - <i>trans</i> - <i>trans</i>	[Cogly ₂ (NO ₂) ₂] ⁻	4	25	13	—	50	—	—	—
5	<i>cis</i> -NO ₂ - <i>trans</i> -N	[Co(β-ala) ₂ (NO ₂) ₂] ⁻	4	65	60	—	—	70	—	49
6	<i>trans</i> - <i>trans</i> - <i>trans</i>	[Co(β-ala) ₂ (NO ₂) ₂] ⁻	4	38	50	—	—	46	—	43
7	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂ , NH ₃	[Co(NH ₃) ₂ gly(NO ₂) ₂]	5	30	—	32	—	—	60	—
8	<i>trans</i> -NO ₂	[Co(NH ₃) ₂ gly(NO ₂) ₂]	5	18	—	13	—	—	56	—
9	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Coen(β-ala)(NO ₂) ₂]	6	48	—	45	—	—	69	—
10	<i>trans</i> -NO ₂	[Coen(β-ala)(NO ₂) ₂]	6	25	—	15	—	—	43	—
11	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Cotn gly(NO ₂) ₂]	6	49	—	64	81	—	80	—
12	<i>trans</i> -NO ₂	[Cotn gly(NO ₂) ₂]	6	27	—	45	64	—	64	—
13	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Cotn(β-ala)(NO ₂) ₂]	6	60	—	62	90	—	79	—
14	<i>trans</i> -NO ₂	[Cotn(β-ala)(NO ₂) ₂]	6	39	—	40	78	—	59	—
15	<i>cis</i> -NO ₂	[Coen ₂ (NO ₂) ₂] ⁺	7	35	—	30	76	—	78	—
16	<i>trans</i> -NO ₂	[Coen ₂ (NO ₂) ₂] ⁺	7	22	—	17	66	—	70	—
17	<i>cis</i> -NO ₂	[Cotn ₂ (NO ₂) ₂] ⁺	8	51	—	45	86	—	84	—
18	<i>trans</i> -NO ₂	[Cotn ₂ (NO ₂) ₂] ⁺	8	43	—	37	81	—	80	—

* The compositions of solvent systems 1-7 are given in Table I.

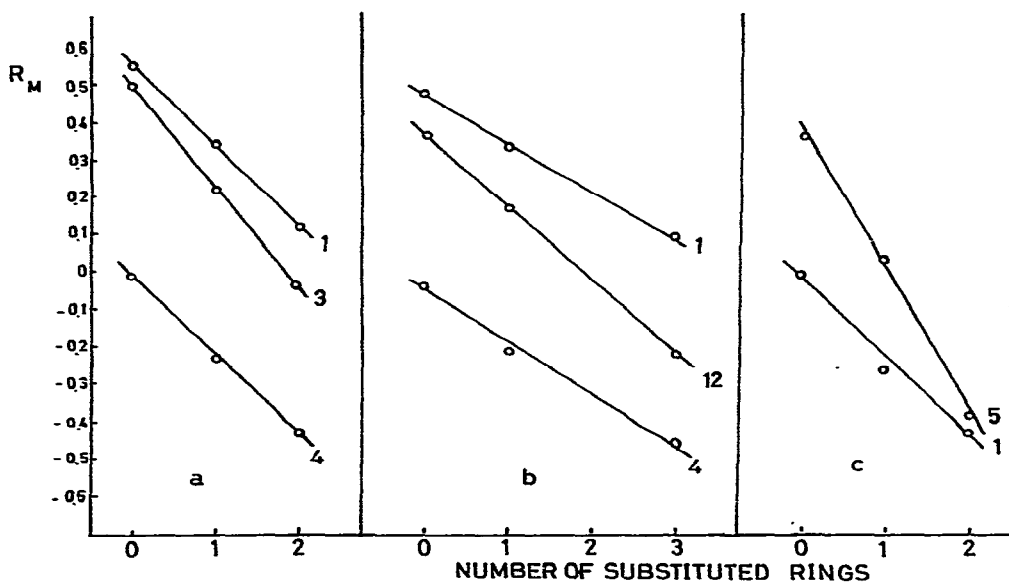


Fig. 1. Dependence of the R_M values on the number of five-membered rings substituted by the corresponding six-membered rings. Complexes: (a) 22-24; (b) 25-27; (c) 3-5 (see Table III). The numbers on the curves refer to the solvent systems used (see Table I).

the position of other ligands cannot be neglected, as neither two *cis*- nor two *trans*-isomers exhibit identical R_F values. The prevailing effect of the position of the nitro groups should probably be ascribed to their pronounced tendency to fill the partly filled p orbitals with electrons from low-energy d orbitals of the central ion, which results in a higher polarity of the *cis*-NO₂ isomer compared with the corresponding *trans*-isomer.

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

In order to study the effect of the chelate ring size on the R_F values of complex compounds, we chromatographed 35 cobalt(III) complexes containing five-membered,

TABLE III
EFFECT OF CHELATE RING SIZE ON R_F VALUES

No.	Isomer	Complex	Ref.	$R_F \times 100^*$											
				1	2	3	4	5	8	9	10	11	12		
1		[Cogly(NO ₂) ₄] ²⁻	9	22	54	31	—	—	76	—	—	—	—		
2		(β-ala)	9	39	61	40	—	—	78	—	—	—	—		
3	<i>cis</i> -NO ₂ - <i>trans</i> -N	[Cogly ₂ (NO ₂) ₂] ⁻	4	53	56	—	—	30	58	—	—	—	—		
4	<i>cis</i> -NO ₂ - <i>trans</i> -N	gly(β-ala)	6	65	—	—	—	48	—	—	—	—	—		
5	<i>cis</i> -NO ₂ - <i>trans</i> -N	(β-ala) ₂	4	73	—	—	—	71	—	—	—	—	—		
6	<i>trans</i> - <i>trans</i> - <i>trans</i>	[Cogly ₂ (NO ₂) ₂] ⁻	4	29	34	14	—	—	33	—	—	—	—		
7	<i>trans</i> - <i>trans</i> - <i>trans</i>	(β-ala) ₂	4	36	54	27	—	—	48	—	—	—	—		
8	<i>cis</i> -O- <i>trans</i> -NH ₂	[CoNH ₃ gly ₂ NO ₂]	5	23	—	—	53	—	—	24	30	15	—		
9	<i>cis</i> -O- <i>trans</i> -NH ₂	(β-ala) ₂	5	43	—	—	80	—	—	32	55	18	—		
10	Meridional(1,2,6-)	[CoNH ₃ gly(NO ₂) ₃] ⁻	10	44	—	—	75	—	—	53	18	44	—		
11	Meridional(1,2,6-)	(β-ala)	5	57	—	—	86	—	—	65	25	45	—		
12	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂ , NH ₃	[Co(NH ₃) ₂ gly(NO ₂) ₂]	5	30	—	—	68	—	—	36	35	47	—		
13	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂ , NH ₃	(β-ala)	5	41	—	—	82	—	—	62	40	48	—		
14	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Coengly(NO ₂) ₂]	7	37	9	—	71	—	—	—	—	—	—		
15	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	(β-ala)	6	48	15	—	86	—	—	—	—	—	—		
16	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	[Cotngly(NO ₂) ₂]	6	49	—	—	81	—	—	53	64	71	—		
17	<i>cis</i> -NO ₂ - <i>trans</i> -NH ₂	(β-ala)	6	60	—	—	90	—	—	65	65	78	—		
18	<i>trans</i> -NO ₂	[Cotngly(NO ₂) ₂]	6	27	—	—	64	—	—	44	49	56	—		
19	<i>trans</i> -NO ₂	(β-ala)	6	39	—	—	78	—	—	60	61	51	—		
20	<i>cis</i> -NO ₂	[Coen ₂ (NO ₂) ₂] ⁺	7	35	—	30	76	—	—	—	—	—	—		
21	<i>cis</i> -NO ₂	tn ₂	8	51	—	45	86	—	—	—	—	—	—		
22	<i>trans</i> -NO ₂	[Coen ₂ (NO ₂) ₂] ⁺	7	22	—	24	53	—	—	—	—	—	—		
23	<i>trans</i> -NO ₂	entn	6	31	—	38	63	—	—	—	—	—	—		
24	<i>trans</i> -NO ₂	tn ₂	8	43	—	52	73	—	—	—	—	—	—		
25	Meridional(1,2,6-)	[Cogly ₃]	11	25	20	3	52	—	10	—	—	—	30		
26	Meridional(1,2,6-)	[Cogly ₃ (β-ala)]	12	32	—	—	62	—	—	—	—	—	46		
27	Meridional(1,2,6-)	(β-ala) ₃	13	45	31	10	74	—	22	—	—	—	62		
28	Facial(1,2,3-)	[Cogly ₃]	11	26	2	—	—	—	2	—	—	—	—		
29	Facial(1,2,3-)	(β-ala) ₃	13	44	12	—	—	—	16	—	—	—	—		
30	<i>trans</i> -N	[Cooxgly ₂] ⁻	14	13	19	—	—	—	—	—	—	—	—		
31	<i>trans</i> -N	(β-ala) ₂	15	34	23	—	—	—	—	—	—	—	—		
32	C ₂ - <i>cis</i> -N	[Cooxgly ₂] ⁻	14	31	46	—	—	—	—	—	—	—	—		
33	C ₂ - <i>cis</i> -N	(β-ala) ₂	15	53	51	—	—	—	—	—	—	—	—		
34		[Coox ₂ gly] ²⁻	16	37	6	—	—	—	—	—	—	—	—		
35		(β-ala)	16	49	8	—	—	—	—	—	—	—	—		

* The compositions of solvent systems 1-5 and 8-12 are given in Table I.

five- and six-membered or six-membered aminocarboxylato (glycine and/or β -alanine), and diamine (ethylenediamine and/or 1,3-trimethylenediamine) chelate rings, respectively. The chromatography was carried out with 10 solvent systems, some of which had been used for the previously described separation of *cis*- and *trans*-isomers. As can be seen from Table III and Fig. 1, it has been established that in all instances an increase in the chelate ring size results in higher R_F values and that there is a linear dependence between the R_M values and the number of five-membered rings substituted by the corresponding six-membered rings. A similar dependence of R_M values on the number of substituted five-membered chelate ligands of one type (ethylenediamine) by another type of five-membered chelate ligand (propylenediamine* or α, α' -dipyridyl) in cobalt(III) complexes has been recently established by Lederer¹⁷.

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* 1,2-Diaminopropane.