Short Communication

Simultaneous effect of geometrical isomerism and chelate ring size of tris(aminocarboxylato)cobalt(III) complexes on their behaviour in thin-layer chromatography on silica gel and alumina

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ABSTRACT

The simultaneous effects of geometrical isomerism and chelate ring enlargement of octahedral complexes on their R_F values obtained by chromatographing twelve isomers of complexes of the general formula $[Co(gly)_{3-x}(\beta\text{-ala})_x]$ (n = 0–3; glyH = glycine; β-alaH = β-alanine) on thin layers of silica gel and alumina by using five monocomponent solvent systems was investigated. It was found that in most instances the effect of the ring size was predominant. Within the series of facial or meridional isomers it was established that with the enlargement of the chelate ring the R_F values of the complexes decreased on silica gel but increased on alumina, which was ascribed to the formation of hydrogen bonds of different strengths between the complexes and the adsorbent.

INTRODUCTION

In earlier work we investigated the effects of geometrical isomerism [1,2] and the chelate ring size [3,4] of transition metal complexes on their behaviour in thin-layer chromatography on silica gel. It was found that when monocomponent solvent systems were applied, lower R_F values were obtained for the *cis* isomers than for the corresponding *trans* isomers. Also, there is a linear dependence between the number of five-membered rings substituted by six-membered rings and the R_M values of the corresponding complexes. Finally, an analogous dependence was established between the chelate diamine ring size and the R_F values of complexes containing five-, six- and seven-membered rings.

Continuing these investigations, in this work we studied the simultaneous effect of both of these factors on the behaviour of tris(aminocarboxylato)cobalt(III) complexes in thin-layer chromatographic (TLC) separations on silica gel and alumina. The complete series of twelve tris(aminocarboxylato)cobalt(III) complexes, which are formed by glycinato and β-alaninato chelate ligands, were considered (Fig. 1). This study is of interest for cases in which both of these factors are operating, as then it is uncertain which regularity (or whether any) will be manifested.

EXPERIMENTAL

Syntheses of the investigated complexes were carried out according to the procedure described previously [5].

Chromatographic separations were performed by the ascending chromatographic method on thin-layers of silica gel (H and G Type 60) and neutral alumina (Type 60/E) from Merck (Darmstadt, Germany) by using five monocomponent solvent systems (Table I). The working technique was described previously [3]. The reproducibility of R_F values was ± 0.03.

The solubilities of complexes were determined as described previously [2].

RESULTS AND DISCUSSION

As can be seen from Table II, it was established that in all instances the facial (fac) isomers exhibit lower R_F values (or the same R_F values within the
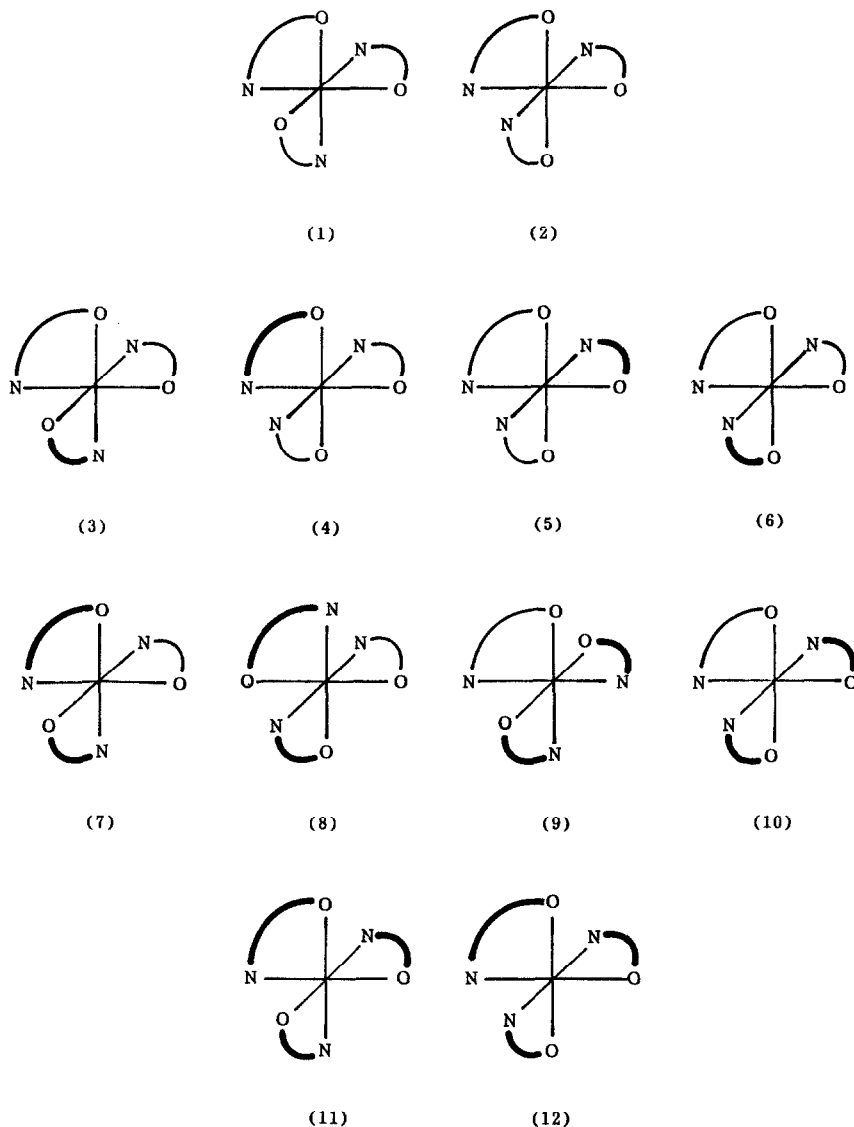

Fig. 1. Tris(aminocarboxylato)cobalt(III) complexes which are formed by glycinato and β-alaninato chelate ligands. β-Alaninato chelate is marked by thick lines; numbers of complexes as in Table II.

TABLE I

SOLVENTS USED

No.	Composition	Development time	
		Silica gel	Alumina
1	Distilled water	35 min	15 min
2	Methanol	50 min	30 min
3	1,2-Propanediol	16 h	15 h
4	1,3-Propanediol	24 h	22 h
5	Ethylene glycol	11 h	17 h

limits of the experimental error) in comparison with the meridional (*mer*) isomers of the same composition. These findings represent an extension of the earlier proposed rule [1,6] which related only to pairs of facial–meridional isomers.

Successive replacement of the glycinato ligand (which forms a five-membered ring with cobalt atom) by a β-alaninato ligand (which forms a six-membered ring) within a series of facial or meridional isomers resulted in decreasing R_F values on thin layers of silica gel (Table II), which is also in accordance with our previously proposed rule [3]. In contrast, on thin layers of alumina a reverse order was observed (Table II), which had not previously been described in the literature. In order to explain this difference, we assumed that in the course of separation of complexes on silica gel hydrogen bonds are formed between hydrogens of silanol groups of the adsorbent and highly electronegative oxygens from the carboxylato groups of the ligand; on thin layers of alumina, however, hydrogen bonds are formed between hydrogens of the amino group of the aminocarboxylato ligands and oxygens of the adsorbent [7]. In connection with the latter it should be pointed out that the glycinato and β-alaninato chelates exhibit differences in the ability for coordinate bond formation, whereby the β-alaninato chelate is a considerably weaker ligand than the glycinato chelate, although it is a stronger

TABLE II

R_F VALUES OF THE INVESTIGATED COMPLEXES

No.	Complex composition[a]	Complex isomers	$R_F \times 100$[b]											
			Silica gel[c]							Alumina				
			1		2	3		4	5	1	2	3	4	5
			H	G	G	H	G	G	G					
1	[Co(gly)$_3$]	fac-	95	89	—	—	39	38	94	93	2	23	2	83
2		mer-	96	97	40	72	72	66	98	94	5	54	14	90
3	[Co(gly)$_2$ β-ala]	fac-	87	86	—	43	34	35	90	95	4	44	7	82
4		trans-(N$_5$)	88	93	28	58	66	54	92	97	5	55	15	86
5		trans-(O$_5$)	92	96	36	68	74	65	89	97	7	67	18	88
6		trans-(N$_5$,O$_5$)	89	92	27	63	70	52	96	95	12	76	26	93
7	[Co gly (β-ala)$_2$]	fac-	79	75	—	36	18	34	—	94	5	46	9	86
8		trans-(N$_6$,O$_6$)	84	88	25	56	63	47	81	99	10	88	23	88
9		trans-(O$_6$)	82	85	21	47	53	45	76	98	14	93	41	93
10		trans-(N$_6$)	76	86	19	41	48	44	90	98	21	94	45	94
11	[Co (β-ala)$_3$]	fac-	64	79	—	18	2	32	77	95	13	73	33	91
12		mer-	76	79	19	40	46	33	74	98	33	95	64	95

[a] glyH = glycine; β-alaH = β-alanine.
[b] The compositions of solvent systems 1–5 used are given in Table I.
[c] H = Silica gel H; G = silica gel G.

base [8], *i.e.*, a potentially better bidentate ligand. In case of cobalt(III) complexes, a weaker ligand field of the β-alaninato chelate relative to that of glycinato chelate is clearly observed in electronic absorption [9] and ^{59}Co NMR spectra [10].

Also, a considerably smaller coordination shift is observed in the ^{15}N NMR spectrum of the amino group nitrogen of the β-alaninato than the glycinato ligands, and they may be correlated with a weaker link between the metal and the ligand [11]. Such behaviour is due to the steric hindrance appearing in the course of incorporating the six-membered ring whereby overlapping of metal and ligand orbitals is reduced [12,13]. Therefore, the coordinated β-alaninato ligand which gives off its electrons to the metal to a markedly smaller extent possesses a greater electron density than the coordinated glycinato ligand, which renders it more capable of hydrogen bonding through the oxygen of the carboxylic group (in the case of silica gel), but less capable of hydrogen bond formation through the hydrogen of the amino group (in the case of alumina).

The geometrical isomers of mixed complexes of the same composition exhibit the same order (within the limits of the experimental error) with all the solvent systems used in TLC separations on alumina, which is not the case on silica gel (Table II), which could be atributted to the solvent effects [14]. Thus in the investigated systems solute–solvent interaction cannot be neglected because of the possible hydrogen bond formation between the solvent and solute molecules.

When considering the R_F values of all twelve isomers of the investigated complexes on both adsorbents (Table II), it is seen that as a rule (within the limits of experimental error and except in 12% of cases on silica gel and 9% of cases on alumina), with increasing number of glycinato ligands substituted by the β-alaninato ligands the R_F values of the complexes decrease on silica gel but increase on alumina, regardless of the geometrical isomerism of the complex. In connection with this, it is worth mentioning that the aforesaid deviations appear mostly with facial isomers, which probably may be ascribed to their relatively low solubility. On the basis of these results, it may be concluded that with the investigated complexes the predominant effect on the R_F values is the chelate ring size relative to the effect of geometrical isomerism.

We also attempted to correlate the R_F values of isomers by using methanol as the solvent system with their solubilities in methanol. On the basis of the results obtained (Table III), it is evident that the solubilities of the facial–meridional pairs are in accordance with the R_F values obtained on both adsorbents. Thus the facial isomers are less soluble and exhibit lower R_F values than the meridional isomers of the same composition. These findings are also in agreement with the fact that the facial isomers are more polar than the meridional isomers and are therefore more strongly adsorbed.

However data on the solubilities (Table III) do not correspond to R_F values of complexes containing chelate rings of different size, or to R_F values of geometrical isomers of mixed complexes of the same composition obtained by TLC separations on both adsorbents, which means that the solubility is not the major factor affecting the R_F values.

Finally, we compared the R_F values of the investigated complexes obtained by TLC on silica gel H using water with the order of their elution from a column of a cationic exchanger in the hydrogen form [5]. In both instances an adsorption separation mechanism is expected, as neutral complexes are separated with water, which represents monocomponent solvent system. From Table II it can be concluded that in most instances a similar order of R_F values was found with other monocomponent organic solvent systems, suggesting the same separa-

TABLE III

SOLUBILITY (mmol/dm^3) AND R_F VALUES OF SOME OF THE INVESTIGATED COMPLEXES IN METHANOL

Complex[a]	Solubility	$R_F \times 100$	
		Silica gel G	Alumina
fac-[Co(gly)$_3$]	2.1	0	2
fac-[Co(gly)$_2\beta$-ala]	4.7	0	4
fac-[Co(β-ala)$_3$]	4.3	0	13
mer-[Co(gly)$_3$]	5.7	40	5
trans-(O$_5$)-[Co(gly)$_2\beta$-ala)	6.4	36	7
trans-(N$_6$,O$_6$)-[Cogly(β-ala)$_2$]	5.8	25	10
trans-(N$_6$)-[Cogly(β-ala)$_2$]	3.2	19	21
mer-[Co(β-ala)$_3$]	13.0	19	33

[a] Abbreviations as in Table II.

TABLE IV

COMPARISON OF THE ORDER OF ELUTION OF THE INVESTIGATED COMPLEXES FROM A CATION-EXCHANGE COLUMN IN H^+ FORM WITH THE R_F VALUES OBTAINED BY THEIR CHROMATOGRAPHY ON THIN LAYER OF SILICA GEL H WITH DISTILLED WATER

Cation-exchange column in hydrogen form [5][a]	$R_F \times 100$
mer-[Co(gly)$_3$]	96
fac-[Co(gly)$_3$]	95
trans-(N_5,O_5)- [Co(gly)$_2$ β-ala]	89
trans-(N_5)-[Co(gly)$_2$ β-ala]	88
trans-(O_5)-[Co(gly)$_2$ β-ala]	92
trans-(O_6)-[Cogly(β-ala)$_2$]	82
fac-[Co(gly)$_2$ β-ala]	87
trans-(N_6)- [Cogly(β-ala)$_2$]	76
trans-(N_6,O_6)-[Cogly(β-ala)$_2$]	84
mer-[Co(β-ala)$_3$]	76
fac-[Co(β-ala)$_3$]	64

[a] Abbreviations as in Table II.

tion mechanism. As can be seen from Table IV, the order of separation on the column is also dependent mainly on the chelate ring size and not on the effect of the geometrical isomerism of complexes, although the order of elution from the column is not identical with the order obtained on this layers of silica gel. It seems that these differences are due to the fact that silica gel has several active centres [15], which is not the case with the ion exchanger used. Consequently, these results support our hypothesis that the investigated isomers are separated on thin layers of silica gel by the mechanism of hydrogen bond formation, in view of the fact that they behave similarly on a cation exchanger in the hydrogen form.

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