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Short communication

Effect of the chelate ring size of diamine–Co(III) complexes on their hR_F values obtained under salting-out thin-layer chromatography conditions

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Abstract

The effect of the chelate ring size of diamine Co(III) complexes under salting-out thin-layer chromatography (TLC) conditions was investigated. For that purpose, 16 neutral and cationic complexes containing from five- to seven-membered diamine chelate rings were chromatographed on the thin layers of silica gel, cellulose and polyacrylonitrile sorbents. Six aqueous solutions of ammonium sulphate at various concentrations were used as solvent systems. In all of the instances studied, it was established that hR_F values decrease with increasing ring size. It was also found that the R_M values obtained were a linear function; on the one side, salt concentrations in the chromatographic solvent systems used, and on the other side the diamine chelate ring size. To explain these results, a mechanism based on hydrophobic interaction between the sorbent and sorbate is proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Adsorbents; Diamine complexes; Cobalt complexes; Metal complexes

1. Introduction

The effect of the chelate ring size on Co(III) complexes under planar chromatography conditions was examined in detail in Ref. [1] and on a thin layer of silica gel using monocomponent solvent systems in Ref. [2]. It was established that, in all cases, except when water was used as a solvent in thin-layer chromatography (TLC) on silica gel, hR_F values of the examined complexes regularly increase with enlargement of the chelate ring size. Such a behaviour of the above complexes under paper chromatography conditions was explained by the normal-phase partition mechanism. On the other hand, it was assumed that the separation of these compounds under TLC conditions on silica gel was based on the solvation mechanism (positive solvation

effect in organic solvents, and negative in water as the mobile phase) [3].

In addition, in the separation on a thin layer of polyacrylonitrile (PAN) sorbent of *cis-trans* isomeric Co(III) complexes containing five- and six-membered diamine rings [4], it was noticed that enlargement of the ring size results in increased retention, although the differences in the hR_F values were small.

In this work, we intended to investigate the effect of the chelate ring size of diamine Co(III) complexes on their behaviour under salting-out (SO) chromatography conditions. This typically reversed-phase (RP) chromatographic method is based on the use of moderately to strongly concentrated aqueous solutions of salts as mobile phases. The high polarity of these solvents enables the use of polar sorbents in RP-TLC, as, for example, non-modified silica gel. Since the first works of Lederer and coworkers, [5,6]

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until the present time, besides its use for separation of a great number of organic substances, SO–TLC has been also used for the separation of some Co(III) complexes [7–12]. As the effect of the chelate ring size of diamine metal complexes under these conditions has not been considered in detail, the neutral and cationic type of Co(III) complexes containing from five- to seven-membered rings were chosen for the above-mentioned effect to be examined. Thin layers of three sorbents were chosen for the separation, i.e., silica gel, cellulose and PAN sorbent, which differ from each other.

2. Experimental

2.1. Syntheses

All of the complexes investigated (Tables 1–3) were synthesized according to procedures described in the literature.

2.2. Chromatography

The thin layers of silica gel H (Merck, Darmstadt, Germany) and PAN sorbent were prepared as de-

scribed in our earlier papers [2,4]. In addition, chromatographic separations were carried out on a thin layer of cellulose as well (Art. 5552, Merck).

Ammonium sulphate (Merck) of analytical grade was used in the preparation of aqueous solutions of various concentrations (Tables 1–3). Before development, the spotted plates were placed in a chromatographic chamber saturated with vapour of the solvent system being used for 15 min. The solvent front travelled about 5 cm. Detection was performed by keeping the plates above a 2-M ammonium sulphide solution for 10 min. All investigations were carried out at room temperature ($22 \pm 1^\circ\text{C}$).

Results and discussion

As can be seen from Tables 1–3, the investigation of the effect of diamine chelate ring size on the chromatographic behaviour of Co(III) complexes was performed on cationic and neutral-type complexes containing from five- to seven-membered rings. Due to their good solubility and high SO effect [7,8], the aqueous solutions of ammonium sulphate of

Table 1
 hR_F values of the complexes investigated, obtained on silica gel

No.	Complex ^a	Isomer	Ref.	Content of ammonium sulphate in solvent system					
				0.92 0.50	1.88 1.00	2.89 1.50	3.97 2.00	5.12 2.50	6.36 mol% 3.00 mol/dm ³
1	[Co(NO ₂) ₂ en ₂] ⁺	<i>trans</i> -(NO ₂)	13	73	68	65	61	57	53
2	[Co(NO ₂) ₂ tn ₂] ⁺		14	60	50	51	47	43	37
3	[Co(NO ₂) ₂ tmd ₂] ⁺		15	45	41	39	33	29	23
4	[Co(NO ₂) ₂ en ₂] ⁺	<i>cis</i> -(NO ₂)	13	87	84	80	78	74	68
5	[Co(NO ₂) ₂ tn ₂] ⁺		14	68	64	60	55	51	47
6	[Co(NO ₂) ₂ tmd ₂] ⁺		15	53	44	40	36	34	31
7	[Co en ₃] ³⁺		16	86	84	84	79	76	73
8	[Co tn ₃] ³⁺		16	70	65	59	57	53	51
9	[Co tmd ₃] ³⁺		17	43	41	37	33	30	27
10	[Co(NO ₂) ₂ (<i>R</i> -ala) en]	<i>cis</i> -(NO ₂)	18	85	82	78	74	68	61
11	[Co(NO ₂) ₂ (<i>R</i> -ala) tn]		18	73	68	69	56	50	43
12	[Co(NO ₂) ₂ (<i>R</i> -ala) tmd]		15	63	57	45	35	35	28
13	[Co(NO ₂) ₂ gly tn]	<i>cis</i> -(NO ₂) <i>trans</i> -(NH ₂)	19	73	72	69	66	64	61
14	[Co(NO ₂) ₂ gly tmd]		15	67	64	60	58	54	45
15	[Co(NO ₂) ₂ gly en]	<i>trans</i> -(NO ₂)	15	96	97	96	95	93	90
16	[Co(NO ₂) ₂ gly tn]		20	79	75	71	66	61	57

^a en=1,2-diaminoethane; tn=1,3-diaminopropane; tmd=1,4-diaminobutane; glyH=glycine; *R*-ala H=(*R*)-alanine.

Table 2
 hR_F values of the complexes investigated, obtained on PANS

No.	Complex ^a	Isomer	Ref.	Content of ammonium sulphate in solvent system					
				0.92 0.50	1.88 1.00	2.89 1.50	3.97 2.00	5.12 2.50	6.36 mol% 3.00 mol/dm ³
1	[Co(NO ₂) ₂ en ₂] ⁺	<i>trans</i> -(NO ₂)	13	95	94	91	87	83	77
2	[Co(NO ₂) ₂ tn ₂] ⁺		14	87	84	78	73	65	60
3	[Co(NO ₂) ₂ tmd ₂] ⁺		15	51	44	38	33	26	22
4	[Co(NO ₂) ₂ en ₂] ⁺	<i>cis</i> -(NO ₂)	13	89	86	82	80	76	70
5	[Co(NO ₂) ₂ tn ₂] ⁺		14	74	69	66	60	55	50
6	[Co(NO ₂) ₂ tmd ₂] ⁺		15	46	44	34	30	24	20
7	[Co en ₃] ³⁺		16	F	F	F	F	F	F
8	[Co tn ₃] ³⁺		16	F	F	F	F	F	F
9	[Co tmd ₃] ³⁺		17	F	F	F	F	F	F
10	[Co(NO ₂) ₂ (<i>R</i> -ala) en]	<i>cis</i> -(NO ₂)	18	86	82	78	74	70	66
11	[Co(NO ₂) ₂ (<i>R</i> -ala) tn]		18	80	75	70	64	60	55
12	[Co(NO ₂) ₂ (<i>R</i> -ala) tmd]		15	70	66	62	58	53	50
13	[Co(NO ₂) ₂ gly tn]	<i>cis</i> -(NO ₂) <i>trans</i> -(NH ₂)	19	94	89	86	83	77	73
14	[Co(NO ₂) ₂ gly tmd]		15	84	81	78	74	68	64
15	[Co(NO ₂) ₂ gly en]	<i>trans</i> -(NO ₂)	15	90	87	82	78	72	67
16	[Co(NO ₂) ₂ gly tn]		20	85	81	77	71	66	60

^a See Table 1.

^b F=Solvent system front.

various concentrations were used as solvent systems in these separations.

The hR_F values obtained are given in Tables 1–3. As can be seen, in all of the cases where separation occurs, the hR_F values of the complexes decrease with enlargement of the diamine ring size (RP

sequence). Such chromatographic behaviour for the examined complexes is in agreement with the results obtained in separations of other organic and inorganic substances under SO–TLC conditions. Namely, enlargement of the ring leads to an increase in the nonpolar hydrocarbon part of the complex, resulting

Table 3
 hR_F values of the complexes investigated, obtained on cellulose

No.	Complex ^a	Isomer	Ref.	Content of ammonium sulphate in solvent system					
				0.92 0.50	1.88 1.00	2.89 1.50	3.97 2.00	5.12 2.50	6.36 mol% 3.00 mol/dm ³
1	[Co(NO ₂) ₂ en ₂] ⁺	<i>trans</i> -(NO ₂)	13	94	93	93	92	91	88
2	[Co(NO ₂) ₂ tn ₂] ⁺		14	94	93	92	90	87	83
3	[Co(NO ₂) ₂ tmd ₂] ⁺		15	94	91	89	83	77	68
4	[Co en ₃] ³⁺		16	F	F	F	F	F	F
5	[Co tn ₃] ³⁺		16	F	F	F	F	F	F
6	[Co tmd ₃] ³⁺		17	F	F	F	F	F	F
7	[Co(NO ₂) ₂ glyen]	<i>trans</i> -(NO ₂)	15	90	92	90	86	85	80
8	[Co(NO ₂) ₂ glytn]		20	90	89	88	82	80	72
9	[Co(NO ₂) ₂ glytmd]		15	90	88	87	80	76	64
10	[Co(NO ₂) ₂ (<i>R</i> -ala)en]	<i>cis</i> -(NO ₂)	18	93	90	87	84	81	77
11	[Co(NO ₂) ₂ (<i>R</i> -ala)tn]		18	92	90	86	82	76	72
12	[Co(NO ₂) ₂ (<i>R</i> -ala)tmd]		15	91	89	82	78	72	64

^a See Table 1.

^b F=Solvent system front.

in stronger nonspecific hydrophobic interactions with hydrophobic parts of the sorbent, which is a predominant separation mechanism in this chromatographic method. In all cases, a linear dependence was also found between chelate ring size and the corresponding R_M values of the investigated complexes. Some of those straight lines are shown in Fig. 1.

In addition, from the results obtained, it can be seen that in most cases an increase in salt concentration causes a decrease in hR_F values of the examined complexes (SO effect). Such chromatographic behaviour is in agreement with the results obtained in SO-TLC of the other transition metal complexes, and is explained by the increase in the surface tension of the solvent with the increase in the concentration of salt [8,21]. The above-mentioned effect was lacking in the chromatography of tris(ethylenediamine)-Co(III) complexes on PAN sorbent and thin layers of cellulose (Tables 2 and 3, complexes 4–6). This could be explained by the differences in the polarities of the sorbents used, namely, it is possible for the mentioned complexes to sorb from a very polar solvents only on a very polar silica gel. Besides, some negligibly low deviations from the said regularity occur in two cases by using a solvent containing the lowest salt content for the

complex separation containing the lowest hydrophobic part (Tables 1 and 3, complexes 15 and 7, respectively). As is known [8], such deviations in the cases of the weakest nonspecific hydrophobic interactions are caused by the stronger effect of specific sorbent-sorbend actions.

In all of the cases examined, there was a linear dependence between the R_M values of the complexes investigated and mol% of ammonium sulphate in the solvent system (Fig. 2). The corresponding parameters of the linear regression analysis are given in Table 4.

Since the straight line slopes represent the criterion of SO efficiency, m [8], from the data given in Table 4, some specific characteristics of the sorbent used can be seen. Thus, it is seen that the lowest SO efficiency on the thin layers of silica gel is in the case of tris(ethylenediamine)-Co(III) complexes. Moreover, there was considerably greater SO efficiency for neutral-type complexes than for cationic complexes. In contrast, on thin layers of PAN sorbent, which, due to the negative charge presence localised on cyano groups, can bring about specific interactions with cationic sorbates [4,22], the SO efficiency of cationic complexes is greater than that for neutral-type complexes. With regard to the SO effect on a thin layer of cellulose, no important

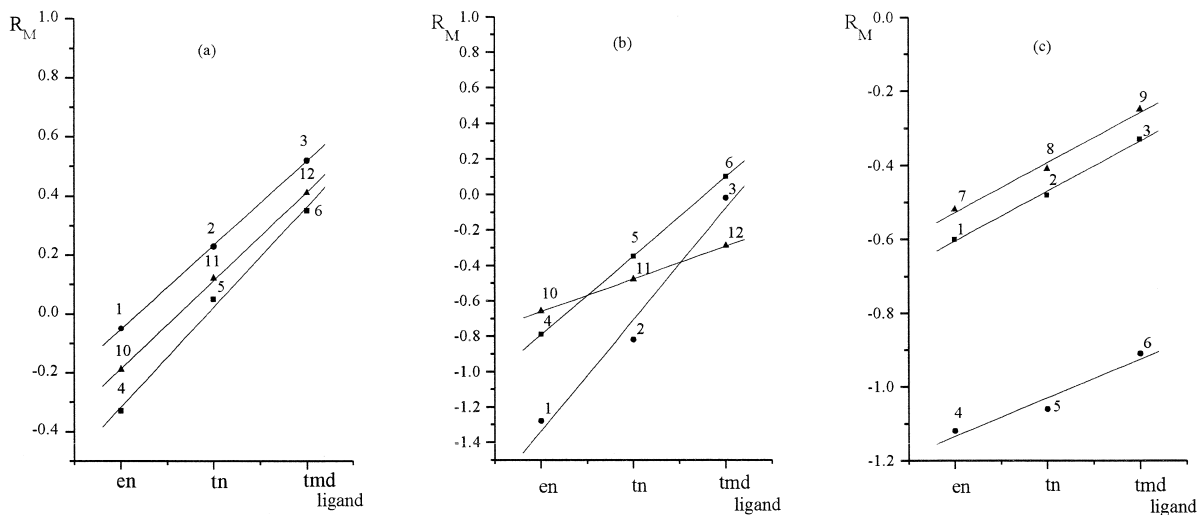


Fig. 1. Dependence of the R_M values of the complexes investigated on the chelate ring size: (a) silica gel; concentration, mol/dm³; (b) PAN, for complexes 1–6 and 10–12; concentration, 1 and 0.5 mol/dm³, respectively; (c) cellulose, for complexes 1–3, 7–9 and 4–6; concentration, 3 and 1.5 mol/dm³, respectively. The numbers adjacent to the points denote the numbers of the complexes in Tables 1–3.

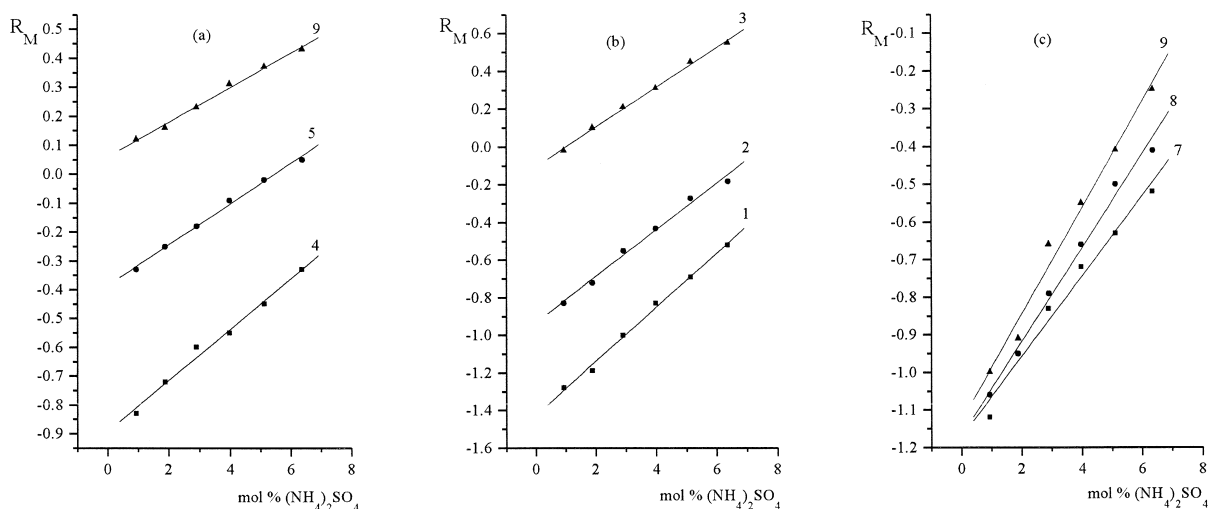


Fig. 2. Dependence of the R_M values of the investigated complexes on the mol % of ammonium sulphate in the solvent system used on (a) silica gel, (b) PAN and (c) cellulose. The numbers on the right of the lines denote the numbers of the complexes, as given in Tables 1–3.

differences based on the type of complex were found. However, in this case, it was established that the SO efficiency, m , was a linear function of the chelate ring size (Fig. 3). Such regularity, i.e., linear

dependence between m and the number of carbon atoms in the hydrophobic part of a complex was also established in SO–TLC of the mixed aminocarboxylato–Co(III) complexes [9].

Table 4
Parameters of linear correlations^a

Complex ^b	Isomer	Silica gel			PAN sorbent			Cellulose		
		A	B	r	A	B	r	A	B	r
[Co(NO ₂) ₂ en ₂] ⁺	<i>trans</i> -(NO ₂)	-0.47184	0.06788	0.99444	-1.42626	0.14373	0.99671	-1.25549	0.05492	0.96534
[Co(NO ₂) ₂ tn ₂] ⁺		-0.19341	0.06492	0.95915	-0.93043	0.12368	0.99491	-1.30340	0.09330	0.99406
[Co(NO ₂) ₂ tmd ₂] ⁺		-0.00247	0.07927	0.99150	-0.09918	0.10445	0.99783	-1.33108	0.15788	0.99779
[Co(NO ₂) ₂ en ₂] ⁺	<i>cis</i> -(NO ₂)	-0.88898	0.08798	0.99479	-0.97227	0.09497	0.99378			
[Co(NO ₂) ₂ tn ₂] ⁺		-0.38214	0.07038	0.99732	-0.51795	0.08305	0.99733			
[Co(NO ₂) ₂ tmd ₂] ⁺		-0.05414	0.06806	0.96093	-0.04148	0.10326	0.99133			
[Co en ₃] ³⁺		-0.86269	0.06812	0.98094						
[Co tn ₃] ³⁺		-0.38833	0.06358	0.97121						
[Co tmd ₃] ³⁺		0.06072	0.05935	0.99702						
[Co(NO ₂) ₂ (R-ala) en]	<i>cis</i> -(NO ₂)	-0.84880	0.10221	0.99948	-0.83606	0.09056	0.98996	-1.17086	0.10630	0.98749
[Co(NO ₂) ₂ (R-ala) tn]		-0.55318	0.10549	0.97460	-0.65808	0.09406	0.99132	-1.16709	0.12439	0.99519
[Co(NO ₂) ₂ (R-ala) tmd]		-0.30547	0.11896	0.96975	-0.41894	0.06871	0.99592	-0.12734	0.14106	0.99213
[Co(NO ₂) ₂ gly tn]	<i>cis</i> -(NO ₂)	-0.48037	0.04547	0.99501	-1.22154	0.13208	0.97467			
	<i>trans</i> -(NH ₂)									
[Co(NO ₂) ₂ gly tmd]		-0.38084	0.06755	0.98117	-0.79934	0.08822	0.99803			
[Co(NO ₂) ₂ gly en]	<i>trans</i> -(NO ₂)				-1.04121	0.12016	0.99452	-1.11946	0.07591	0.91958
[Co(NO ₂) ₂ gly tn]		-0.63782	0.08429	0.99647	-0.83428	0.10618	0.99753	-1.07051	0.09262	0.98096
[Co(NO ₂) ₂ glytmd]								-1.09359	0.11762	0.98745

^a A=intercept; B=slope; r=correlation coefficient.

^b See Table 1.

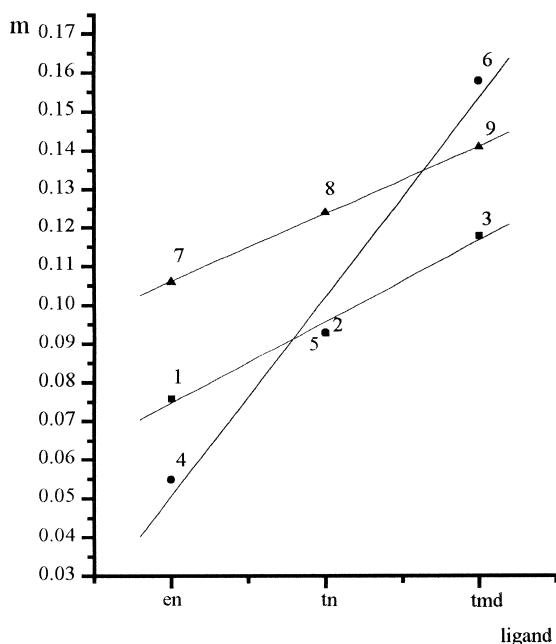


Fig. 3. Dependence of the m values of the investigated complexes on chelate ring size. The numbers adjacent to the points denote the numbers of the complexes as given in Table 3.

On the basis of the results obtained, it could be concluded that all three sorbents, regardless of the considerable differences in their characteristics [4,23], can be successfully used in SO–TLC of metal complexes with various sizes of diamine chelate ring.

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