Note

Dependence of R_F values of cobalt(III) complexes on the size of diamine chelate ligands on silica gel thin layers

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In a previous paper[1] we reported the dependence of the R_F values of cobalt(III) complexes, obtained by thin-layer chromatography (TLC) on silica gel, on the size of the five- and six-membered aminocarboxylato and diamine ligands. It was found that in the TLC separations with monocomponent solvent systems the R_F values of the complexes with aminocarboxylato ligands decrease with increasing chelate ring size. In contrast, the complexes which in addition to aminocarboxylato ligands contained oxalato ligands instead of nitro groups exhibited the reverse order. Finally, in TLC separations of complexes containing diamine ligands the R_F values of the complexes increased with increasing chelate ring size, except when elution was carried out with water, when the reverse order occurred. However, when TLC separations were carried out with multicomponent solvent systems no regularity was observed for any of the aforementioned series. In all instances a linear dependence was found between the number of five-membered rings substituted by six-membered rings and the R_M values of the complexes.

Continuing these investigations, in this study we examined complexes containing seven-membered diamine ligands and possible separation mechanisms.

EXPERIMENTAL

The complexes investigated were prepared according to procedures reported in the literature (Table I). TLC separations on silica gel 60 G (Merck, Darmstadt, F.R.G.) were carried out as described in an earlier paper[1] and the solubility of the complexes was determined as described in a subsequent paper[2].

RESULTS AND DISCUSSION

Twenty-one cationic and neutral cobalt(III) complexes were chromatographed on silica gel thin layers. In addition to the five-, six- or seven-membered diamine ligands, the investigated complexes also contained, except in one instance, glycinato, (R)-alaninato or nitro ligands (Table I). The chromatographic separations were performed with the use of ten monocomponent solvent systems (Table II). As can be seen from Table I, with the application of nine non-aqueous solvent systems the R_F values

TABLE I

R_F VALUES OF THE INVESTIGATED COMPLEXES OBTAINED BY TLC

No.	Isomer	Absolute configuration	Complex*	Ref.	$R_F \times 100$**									
					1	2	3	4	5	6	7	8	9	10
1	cis-(NO₂), trans-(NH₂)-		[Co(NO₂)₂gly en]	3	76	68	—	7	—	—	—	—	—	—
2			tn	4	72	71	—	12	—	—	—	—	—	—
3			tmd	5	68	73	—	21	—	—	—	—	—	—
4	trans-(NO₂)-		[Co(NO₂)₂gly en]	5	81	—	39	4	0	78	—	—	—	—
5			tn	4	72	—	52	11	4	91	—	—	—	—
6			tmd	5	60	—	66	22	7	95	—	—	—	—
7	cis-(NO₂)-	Λ-(+)₅₈₉⁻	[Co(NO₂)₂(R-ala)en]	6	87	63	59	21	0	84	—	—	—	—
8			tn	6	74	68	67	33	7	89	—	—	—	—
9			tmd	5	61	71	75	42	10	92	—	—	—	—
10	cis-(NO₂)-	Δ-(−)₅₈₉⁻	[Co(NO₂)₂(R-ala)en]	6	88	53	40	20	—	87	—	—	—	—
11			tn	6	79	60	53	29	—	90	—	—	—	—
12			tmd	5	67	65	63	43	—	93	—	—	—	—
13	cis-(NO₂)-		[Co(NO₂)₂ en₂]	7	49	—	—	—	—	—	76	12	—	—
14			tn₂	8	26	—	—	—	—	—	78	17	—	—
15			tmd₂	5	17	—	—	—	—	—	80	27	—	—
16	trans-(NO₂)-		[Co(NO₂)₂en₂]⁺	7	45	24	—	—	—	25	79	18	5	57
17			tn₂	8	39	34	—	—	—	30	82	26	11	62
18			tmd₂	5	33	40	—	—	—	32	87	30	26	72
19			[Coen₃]³⁺	9	56	—	—	—	—	—	—	—	—	—
20			tn₃	9	23	—	—	—	—	—	—	—	—	—
21			tmd₃	10	10	—	—	—	—	—	—	—	—	—

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

** The compositions of the solvent systems 1–10 are given in Table II.

TABLE II

SOLVENTS USED FOR TLC

No.	Solvent	Time of development (min)
1	Distilled water	15
2	Methanol	15
3	Ethanol	40
4	Acetone	10
5	Acetylacetone	60
6	1,3-Propandiol	540
7	N,N-Dimethylformamide	10
8	Ethylene glycol monomethyl ether	55
9	Dimethyl sulphoxide	45
10	Glycerine	1080

of the complexes increased with increase in the chelate ring size. In contrast, with the use of water the reverse order was obtained.

In all instances a linear dependence was found between the chelate ring size and the R_M values of the complexes; with non-aqueous solvents this dependence was negative and with water it was positive (Figs. 1 and 2).

We attempted to correlate the results obtained with the solubility of the complexes in the solvent systems used. For this purpose we determined the solubility of three complexes in three solvent systems. As can be seen from Table III, in non-aqueous solvent systems an increase in solubility was followed by an increase in the R_F value, whereas in water this was not so.
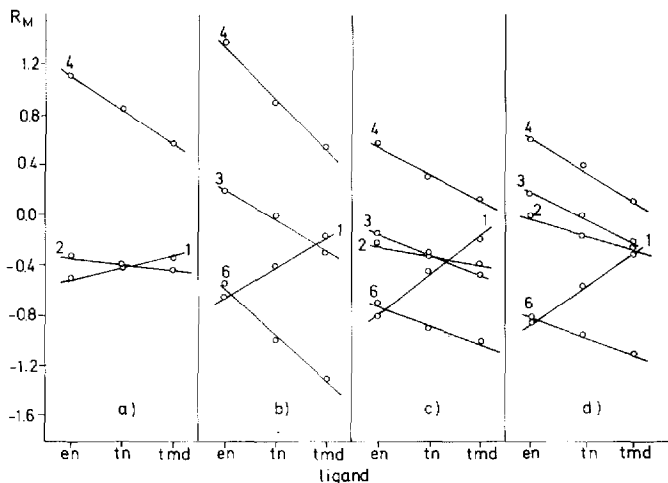

Fig. 1. Dependence of R_M values on the chelate ring size of the following complexes (see Table I): (a) 1–3; (b) 4–6; (c) 7–9; (d) 10–12. The numbers on the lines refer to the solvent systems used (see Table II).
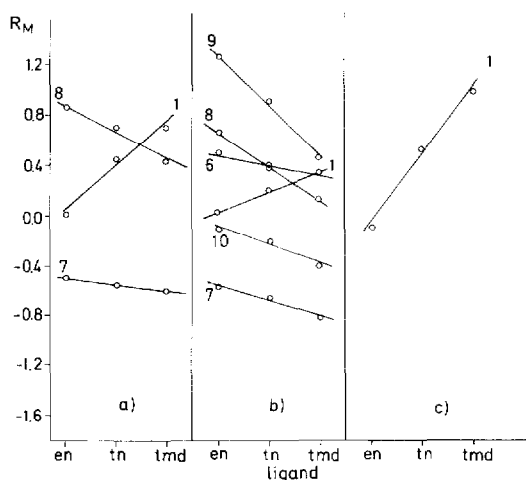
Fig. 2. Dependence of R_M values on the chelate ring size of the following complexes (see Table I): (a) 13–15; (b) 16–18; (c) 19–21. The numbers on the lines refer to the solvent systems used (see Table II).

It is known that when monocomponent solvent systems are used the R_F value of a complex depends on two factors: the strength of the adsorption of the dissolved substance to the adsorbent and the solubility of the substance in the solvent system used. The more strongly the complex is adsorbed the smaller its R_F value should be, whereas with increasing solubility of a complex its R_F value should increase.

As can be seen from Table III, in the chromatographic separations with water the solubility is not of major importance for the separation of the complexes, but rather the strength of their adsorption. The complex with 1,2-diaminobutane displays the lowest R_F value, as it forms the strongest hydrogen bonds. This is in agreement with the fact that in this series 1,4-diaminobutane is the strongest base (Table III).

In contrast, when TLC was carried out with non-aqueous solvent systems the other factor had the major influence, so that the complexes with ligands having larger chelate ring sizes displayed higher R_F values, on account of their higher solubility in the solvent system used.

TABLE III

SOLUBILITIES, R_F AND pK VALUES OF SOME OF THE INVESTIGATED COMPLEXES

Complex*	Solvent						pK_1***	pK_2***
	Water		Methanol		N,N-Dimethylformamide			
	s**	$R_F \times 100$	s**	$R_F \times 100$	s**	$R_F \times 100$		
trans-$[Co(NO_2)_2en]^-$	0.067	45	0.002	24	0.007	79	7.00	10.09
trans-$[Co(NO_2)_2tn]^-$	0.447	39	0.007	34	0.033	82	8.64	10.62
trans-$[Co(NO_2)_2tmd]^+$	0.149	33	0.017	40	0.193	87	9.35	10.80

* Abbreviations as in Table I.
** s = solubility at 20°C (mol/dm³).
*** Taken from ref. 11.

CONCLUSION

The regularities earlier established for cobalt(III) complexes containing five-and/or six-membered chelate rings appear to be valid also for complexes with seven-membered diamine rings. Hence a new possibility is offered for the determination of the composition of the corresponding complexes.

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