Short Communication

Effect of the substituents of β-diketonato ligands on R_F values of tris(chelate) transition metal complexes obtained by normal- and reversed-phase thin-layer chromatography on unmodified silica gel

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ABSTRACT

Three series of tris(β-diketonato) complexes of cobalt(III), chromium(III) and ruthenium(III), in which acetylacetonato ligands were successively replaced with dibenzoylmethanato ligands, were chromatographed on silica gel thin layers and the corresponding mechanisms were considered. The R_F values increased with non-aqueous and decreased with aqueous solvent systems. It was established that unmodified silica gel can be used as a sorbent for both normal- and reversed-phase chromatography of metal complexes. The earlier rule of a linear dependence between the R_M values of tris(chelate) transition metal complexes and the number of substituted chelate ligands by others was extended.

INTRODUCTION

In previous work [1] we studied the effect of the composition of coordinated β-diketonato ligands on the R_F values of transition metal complexes obtained by thin-layer chromatography (TLC) on silica gel. The investigations were carried out with complexes of Co(III), Cr(III), Ru(III) and Rh(III) of the non-electrolyte type containing three identical β-diketonato ligands. On the basis of the results obtained, it was concluded that the complexes investigated, using non-aqueous one- and two-component solvent systems, exhibited the higher R_F values the smaller was the electron density on the oxygen ligator atoms. This was explained by the mechanism of hydrogen bond formation between the oxygen ligator atoms and hydrogen atoms of

the silanol groups of silica gel. However, when the solvent system was acetone–water (60:40, v/v), a reversed elution order of the complexes investigated was obtained, but no adequate explanation has so far given for this phenomenon. Continuing these studies, in this work we investigated, using non-aqueous and aqueous solvent systems, the chromatographic behaviour of three series of tris(chelate) β-diketonato complexes of Co(III), Cr(III) and Ru(III) in which acetylacetonato ligands were successively replaced with dibenzoylmethanato ligands. In this way we wanted to check the earlier established rule [2–5], valid for both paper chromatography [2,3] and TLC [4,5], of a linear dependence between the R_M values and the number n in the series of complexes of the type $[M(chel_1)_n(chel_2)_{3-n}]$, where M denotes an atom of Co(III),

TABLE I

R_F VALUES OF THE COMPLEXES INVESTIGATED BY TLC USING ONE- AND MULTI-COMPONENT SOLVENT SYSTEMS

No.	Complex[a]	Ref.	$R_F \times 100$[b]																	
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	[Co(acac)₃]	6,7	0	0	4	6	0	30	0	24	2	45	0	5	15	14	4	88	81	84	81
2	[Co(acac)₂dibzac]	6,7	3	3	15	16	2	64	2	68	5	59	2	16	45	40	10	65ᶜ	54ᶜ	73ᶜ	72ᶜ
3	[Coacac(dibzac)₂]	6,7	11	10	46	38	5	85	4	96	11	74	7	39	90	76	20	46ᶜ	22ᶜ	55ᶜ	52ᶜ
4	[Co(dibzac)₃]	6,7	41	34	77	68	12	95	8	F	21	84	20	65	Fᵈ	94	39	0	0	0	0
5	[Cr(acac)₃]	8,7	2	0	9	6	0	43	0	32	2	50	0	9	25	19	7	93	77	75	84
6	[Cr(acac)₂dibzac]	8,7	6	4	22	16	2	75	2	86	5	64	3	24	60	55	13	68ᶜ	51ᶜ	64ᶜ	67ᶜ
7	[Cracac(dibzac)₂]	8,7	18	14	53	37	6	86	5	F	12	78	10	50	97	86	23	38ᶜ	19ᶜ	44ᶜ	50ᶜ
8	[Cr(dibzac)₃]	8,7	40	44	77	68	24	F	10	F	25	87	28	75	F	97	45	0	0	0	0
9	[Ru(acac)₃]	9,7	0	0	7	22	0	40	0	30	0	42	5	7	20	14	6	90	87	81	86
10	[Ru(acac)₂dibzac]	9,7	14	11	33	35	4	96	3	96	4	64	11	23	62	76	13	70ᶜ	50ᶜ	71ᶜ	78ᶜ
11	[Ruacac(dibzac)₂]	9,7	34	22	76	50	9	F	5	F	13	80	20	48	90	98	25	46ᶜ	15ᶜ	56ᶜ	59ᶜ
12	[Ri(dibzac)₃]	9,7	59	41	94	66	24	F	9	F	29	88	35	71	F	F	49	0	0	0	0

[a] acac = 2,4-Pentanedionato ion; dibzac = 1,3-diphenyl-1,3-propanedionato ion.
[b] The compositions of the solvent systems are given in Table III.
[c] Small degree of fronting.
[d] F = front.

TABLE II

SLOPES OF THE REGRESSION LINES REPRESENTED FOR THE INVESTIGATED Co(III) CHELATES IN FIG. 2

Central atom	Solvent system																		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Co(III)	2.41	1.17	2.35	1.86	1.52	2.00	1.16	1.74	1.36	1.00	2.01	1.90	3.17	2.44	1.44	−1.71	−2.17	−1.17	−0.55
Cr(III)	1.82	2.32	1.85	1.81	2.17	1.63	1.33	—	1.45	1.00	1.99	1.77	3.64	2.55	1.22	−2.40	−2.10	−1.07	−1.30
Ru(III)	1.28	1.01	2.31	0.82	1.18	—	0.68	—	1.34	1.00	0.99	1.50	2.10	3.35	1.14	−1.43	−2.14	−0.71	−0.85

Cr(III) or Ru(III), $chel_1$ and $chel_2$ represent chelate ligands of the same charge and $n = 0$–3. In addition, we wanted to give an explanation for the reversed elution order of complexes observed previously [1]. Finally, the aim of this work was also to compare the results obtained here with those reported previously [5] in which these complexes were chromatographed on polyacrylonitrile layers.

EXPERIMENTAL

Syntheses

All complexes investigated were obtained by direct synthesis, i.e., by the action of a mixture of acetylacetone and dibenzoylmethane on the corresponding metal ion, whereby in each reaction all four possible complexes of a metal were obtained [6–9].

Chromatography

Chromatographic separations were carried out on silica gel plates (5 × 5 cm) (HPTLC Fertigplatten 60 für die Nano-DC; Merck, Darmstadt, Germany). Standard solutions (2 mg/cm^3) of the tris (β-diketonato) complexes investigated were prepared in chloroform and the plates were spotted

TABLE III

SOLVENT SYSTEMS USED

No.	Composition	Proportions (v/v)
1	Benzene	
2	Toluene	
3	Dichloromethane	
4	Chloroform	
5	Xylene	
6	n-Butyl acetate	
7	1,1-Dichlorethylene	
8	n-Amyl acetate	
9	1,2,3,4-Tetrahydronaphthalene	
10	Toluene–tetrahydrofuran	85:15 (v/v)
11	Toluene–n-hexane	70:30 (v/v)
12	Toluene–dichloromethane	50:50 (v/v)
13	n-Butyl acetate–carbon tetrachloride	30:70 (v/v)
14	n-Butyl acetate–chloroform	30:70 (v/v)
15	Chloroform–carbon tetrachloride	60:40 (v/v)
16	Acetone–water	60:40 (v/v)
17	Ethanol–water	65:35 (v/v)
18	Dioxan–water	60:40 (v/v)
19	Methanol–water	75:25 (v/v)

with 0.2-μl aliquots of freshly prepared solutions. Before development, the spotted plates were placed for 30 min in a chromatotographic chamber (4 × 6 × 10 cm) saturated with vapour of the solvent system being used. All solvents were of analytical-reagent grade. After development, the spots of individual complexes were visible, owing to their natural colours.

RESULTS AND DISCUSSION

As can be seen from Table I, twelve tris(chelate) complexes of Co(III), Cr(III) and Ru(III), of the non-electrolyte type, containing acetylacetonato and/or dibenzoylmethanato ligands, were chromatographed on thin layers of silica gel, with nine one- and ten two-component solvent systems (Table III). The results obtained show that with non-aqueous one-component solvent systems (Table I, Nos. 1–9) the R_F values of metal complexes increase with increasing number of acetylacetonato ligands substituted by dibenzoylmethanato ligands. The same order of complexes was also obtained with slightly polar non-aqueous two-component solvent systems (Table I, Nos. 10–15). These results are in accordance with a specific interaction of these complexes with the sorbent, which involves the formation of hydrogen bonds between the electronegative oxygen ligator atoms of the chelate and hydrogen atoms of the silanol groups of silica gel. Owing to a negative inductive effect of the phenyl group, the electron density on the oxygen atoms of dibenzoylmethane is smaller than those of acetylacetone, which is why in the former instance the hydrogen bonds formed with the sorbent are weaker, causing a greater mobility of these complexes.

If the order of these complexes obtained by TLC on silica gel with slightly polar non-aqueous solvent systems is compared with that obtained on polyacrylonitrile [5], it may be concluded that this order is reversed. The reason is probably that in the former instance the separtion is due to the formation of hydrogen bonds, as already described, whereas in the latter the separation mechanism involves the interaction of π-electrons of aryl-β-diketonato ligands with cyano groups of the sorbent.

When chromatographic separations were carried out with solvents systems containing 25–40% of water, a reversed elution order of complexes relative
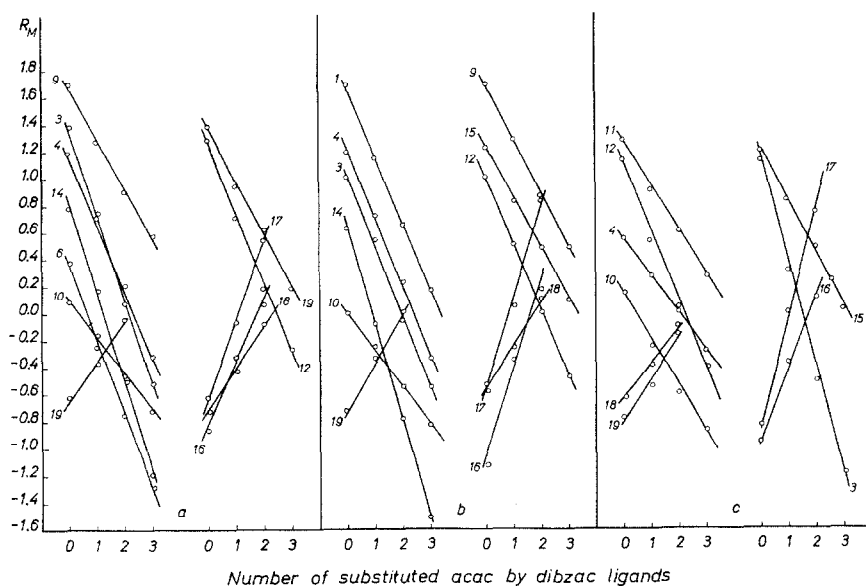
Fig. 1. Dependence of R_M values on the number of 2,4-pentanedionato ligands (acac) substituted by 1,3-diphenyl-1,3-propanedionato ligands (dibzac) in the [M(acac)$_n$(dibzac)$_{3-n}$]-type complexes (n = 0–3). (a) Cobalt(III); (b) chrominum(III); (c) ruthenium (III). The numbers on the lines refer to the solvent system used (see Table III).

to that found when using non-aqueous solvent systems was obtained (Table I, Nos. 16–19). The latter is in accordance with the fact that more polar solutes elute later in normal-phase systems because the stationary phase is more polar than the mobile phase, and polar solutes elute first in reversed-phase systems because the stationary phase is less polar. In this way it was established for the first time that unmodified silica gel can be used as the sorbent for the reversed-phase chromatography of metal complexes.

The same order of complexes was also obtained in previous work [5] on TLC on polyacrylonitrile by the application of aqueous solvent systems, which was also ascribed to non-specific hydrophobic interactions.

This work also extends the above-mentioned rule [2–5] of a linear dependence between the R_M values of tris(chelate) transition metal complexes and the number of substituted chelate ligands by others in chromatographic separations with both non-aqueous and aqueous solvent systems on silica gel (Fig. 1).

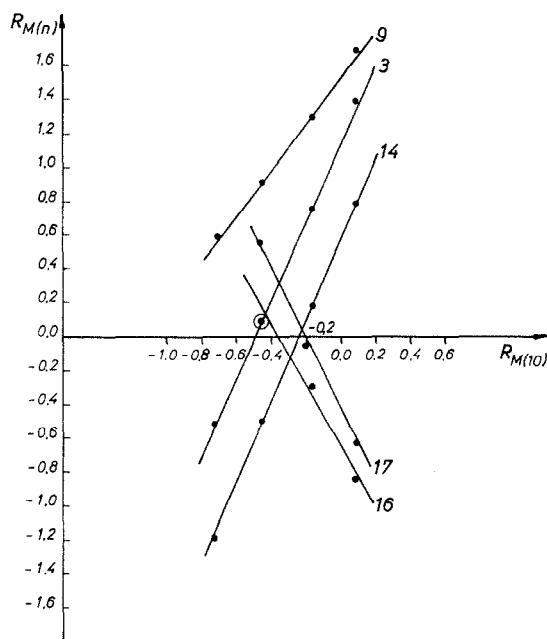In order to represent quantitatively the selectivity differences between some of the solvent systems

Fig. 2. Correlation between the R_M values of the investigated Co(III) chelates obtained on a thin layer of silica gel with a given solvent system and solvent system 10. $R_{M(n)}$ = R_M values obtained with the solvent system shown by the number on the line; see Table III; $R_{M(10)}$ = the same for solvent system 10.

used in this paper, in Fig. 2 the plots of the correlation between the R_M values of the investigated Co(III) complexes, obtained with solvents 3, 9, 14, 16 and 17 (see Table III), and their R_M values obtained with solvent system 10 are given [10]. In addition, in Table II the corresponding slopes for all three of the applied metals are given. As can be concluded from these data, in normal-phase chromatography the highest selectivity is achieved with solvents 13 and 14, and in reversed-phase chromatography with solvent systems 16 and 17.

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