

## Note

### Effect of the composition of coordinated $\beta$ -diketonato ligands on $R_F$ values of transition metal complexes obtained by thin-layer chromatography on silica gel

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The effect of the composition of coordinated  $\beta$ -diketonato ligands on  $R_F$  values of transition metal complexes, obtained by thin-layer chromatography (TLC) on silica gel, has already been investigated.

Dilli and Robards<sup>1</sup> have undertaken an examination of a number of aryl  $\beta$ -diketonates and their chelates in an effort to highlight the effect of certain structural factors during TLC and to compare these with the known gas chromatographic (GC) behaviour. For TLC, air-dried silica gel plates were used and the development was performed by means of solvent systems benzene and benzene–methanol (92:8, v/v). On the basis of the results obtained, the authors concluded that “the trend in  $R_F$  values varied considerably for the different metal ions and a parallel between the TLC and GC behaviour of the chelates is immediately apparent”.

Timerbaev and Petrukin<sup>2</sup> performed chromatographic separations by using only two single component solvent systems (chloroform and diisopropyl ether) keeping a constant humidity in the cylinder in the course of development. Thereby they established that the  $R_F$  values of the complexes investigated increase in the following order of the ligands\*: acac < bzac < dibzac < tfac < hfac. These results were ascribed to the weakening of the strength of adsorption of the complexes to the adsorbent, caused by decreasing oxygen atom electron density. This is due to the effect of substituents attached to the 2,4-pentanedionato ligand.

However, in our earlier investigations on the effect of the composition and structure of metal complexes on their  $R_F$  values<sup>3–5</sup> we have established that the behaviour of complexes may be quite different when, instead of single component solvents, polycomponent solvent systems are used. The reason is that in the latter case, in addition to the adsorption mechanism, a partition separation mechanism may also be involved. This aspect is not well defined in the previously mentioned papers<sup>1,2</sup>. In the first study the authors applied only one single component solvent system and air-dried silica gel plates, which means that their silica gel contained adsorbed water<sup>6</sup>.

\* acac = 2,4-Pentanedionato ion; bzac = 1-phenyl-1,3-butanedionato ion; dibzac = 1,3-diphenyl-1,3-propanedionato ion; tfac = 1,1,1-trifluoro-2,4-pentanedionato ion; tfacbzac = 1-phenyl-4,4,4-trifluoro-1,3-butanedionato ion; hfac = 1,1,1,6,6,6-hexafluoro-2,4-pentanedionato ion; ttfac = 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionato ion.

In the second study the authors performed chromatographic separations with single component solvent systems in an humid atmosphere. That is why we wanted to investigate the aforementioned effect with a greater number of transition metal complexes, using dry single component solvent systems and silica gel. In addition, we wanted to establish whether the previously found regularities hold also when polycomponent solvent systems are applied.

#### EXPERIMENTAL

The complexes investigated were synthesized according to procedures reported in the literature (Table I). Chromatographic separations on thin layers of silica gel (DG; Riedel, Hannover, F.R.G.), as well as the drying of the solvent used, are described in our previous papers<sup>3,7</sup>.

#### RESULTS AND DISCUSSION

As seen from Tables I and II, eighteen complexes of Co(III), Cr(III), Ru(III) and Rh(III) of the non-electrolyte type, containing some of the ligands acac, bzac, dibzac,

TABLE I

$R_F$  VALUES OF COMPLEXES OBTAINED BY TLC ON SILICA GEL USING SINGLE COMPONENT SOLVENT SYSTEMS

No.	Complex	Ref.	$R_F \cdot 100^*$							
			1	2	3	4	5	6	7	8
1	[Co(acac) <sub>3</sub> ]	8	1	23	2	7	2	10	74	2
2	[Co(bzac) <sub>3</sub> ]**	9	13	46	4	13	13	30	87	9
			—	—	—	—	—	51	—	—
3	[Co(dibzac) <sub>3</sub> ]	9	64	83	33	—	64	86	90	55
4	[Co(tfac) <sub>3</sub> ]**	10	68	84	36	36	68	88	96	84
			78	—	41	50	78	—	—	—
5	[Co(tfacbzac) <sub>3</sub> ]	11	87	85	78	70	88	90	—	93
6	[Co(hfac) <sub>3</sub> ]	12	—	96	—	—	—	99	98	98
7	[Cr(acac) <sub>3</sub> ]	13	6	21	3	9	8	16	75	3
8	[Cr(bzac) <sub>3</sub> ]**	9	17	55	11	14	17	39	87	3
			28	67	25	49	28	64	—	—
9	[Cr(dibzac) <sub>3</sub> ]	9	75	89	48	75	76	92	90	67
10	[Cr(tfac) <sub>3</sub> ]**	10	77	94	48	—	78	—	92	67
			85	—	—	—	86	—	—	81
11	[Cr(tfacbzac) <sub>3</sub> ]	11	93	95	88	—	93	—	94	67
12	[Cr(hfac) <sub>3</sub> ]	14	—	96	—	—	—	99	98	89
13	[Ru(acac) <sub>3</sub> ]	15	6	5	—	—	—	11	—	4
14	[Ru(tfac) <sub>3</sub> ]	12	81	82	—	—	—	90	—	53
15	[Ru(hfac) <sub>3</sub> ]	12	86	88	—	—	—	93	—	87
16	[Rh(acac) <sub>3</sub> ]	16	3	13	—	—	—	5	—	1
17	[Rh(bzac) <sub>3</sub> ]**	9	14	15	—	—	—	11	—	10
			28	30	—	—	—	40	—	22
18	[Rh(tfac) <sub>3</sub> ]	10	78	72	—	—	—	88	—	68

\* The compositions of the solvent systems are given in Table III.

\*\* The  $R_F$  values correspond to mixture of the facial and meridional isomers.

TABLE II

$R_F$  VALUES OF COMPLEXES OBTAINED BY TLC ON SILICA GEL USING POLYCOMPONENT SOLVENT SYSTEMS

No.	Complex	$R_F \cdot 100^*$							
		9	10	11	12	13	14	15	16
1	[Co(acac) <sub>3</sub> ]	5	10	6	3	27	25	21	92
2	[Co(bzac) <sub>3</sub> ]**	14	22	20	5	38	26	32	64***
		26	—	36	—	59	—	46	—
3	[Co(dibzac) <sub>3</sub> ]	75	61	86	6	93	49	88	0
4	[Co(tfac) <sub>3</sub> ]**	81	79	83	8	94	61	89	56***
		—	83	—	—	—	73	—	—
5	[Co(tfacbzac) <sub>3</sub> ]	88	90	—	16	95	89	—	—
6	[Co(hfac) <sub>3</sub> ]	89	96	95	17	96	—	94	—
7	[Cr(acac) <sub>3</sub> ]	11	15	16	3	32	5	28	89
8	[Cr(bzac) <sub>3</sub> ]**	13	45	31	5	45	13	34	52***
		30	63	54	—	69	34	52	—
9	[Cr(dibzac) <sub>3</sub> ]	71	77	87	13	92	59	85	0
10	[Cr(tfac) <sub>3</sub> ]**	79	80	87	13	92	62	85	50***
		—	—	—	—	—	75	—	—
11	[Cr(tfacbzac) <sub>3</sub> ]	84	91	97	20	—	96	93	42***
12	[Cr(hfac) <sub>3</sub> ]	93	95	95	21	91	—	96	—
13	[Ru(acac) <sub>3</sub> ]	2	32	10	—	29	3	—	—
14	[Ru(tfac) <sub>3</sub> ]	89	82	86	—	92	73	—	—
15	[Ru(hfac) <sub>3</sub> ]	95	—	—	—	—	90	—	—
16	[Rh(acac) <sub>3</sub> ]	2	31	14	—	29	2	—	—
17	[Rh(bzac) <sub>3</sub> ]	7	44	30	—	49	7	—	—
		20	55	49	—	63	—	—	—
18	[Rh(tfac) <sub>3</sub> ]	85	80	82	—	87	21	—	—

\* The compositions of the solvent systems are given in Table III.

\*\* The  $R_F$  values correspond to mixture of the facial and meridional isomers.

\*\*\* Small degree of fronting.

tfac, hfac or tfacbzac, were chromatographed. The compositions of the eight single component and eight polycomponent solvent systems used are presented in Table III.

From Table I it is seen that in all dry single component solvent systems applied the  $R_F$  values increased in the same order of ligands as established by Timerbaev and Petrukin<sup>2</sup>, who had carried out chromatographic separations with two single component solvent systems but in an humid atmosphere. The same order of complexes was obtained with all polycomponent solvent systems used, except when acetone-water (60:40, v/v) was used (Table II).

On the basis of our results, obtained by the application of dry single component solvent systems and silica gel, it may be concluded that in all cases investigated the complexes are separated by an adsorption mechanism. As to the mechanism operating during the chromatographic development of the complexes by polycomponent solvent systems on dry silicagel, or by single component solvent systems on silica gel containing adsorbed water, nothing can be said with certainty. The reason is that in this case both adsorption and partition are possible. This is in accordance with the fact that the order of the complexes when seven multicomponent solvent systems with

TABLE III  
SOLVENT SYSTEMS USED

No.	Composition	Proportion (v/v)	Time of development (min)
1	Benzene		7
2	Chloroform		7
3	1,2-Dichlorobenzene		17
4	<i>n</i> -Hexane		14
5	Carbon tetrachloride		15
6	Dichloromethane		6
7	Ethyl acetate		8
8	Toluene		8
9	Benzene-dichloromethane	50:50	5
10	Chloroform-carbon tetrachloride	70:30	12
11	Dichloromethane-toluene	70:30	8
12	<i>n</i> -Hexane-carbon tetrachloride	20:80	15
13	Chloroform-dichloromethane	70:30	10
14	Benzene-toluene	50:50	10
15	Chloroform-benzene-dichloromethane	60:20:20	10
16	Acetone-water	60:40	20

small dielectric constants are used is the same as that obtained with single component solvent systems. Contrary to this, using the polycomponent solvent system 16, which contains, besides acetone, 40% (v/v) of water, the above mentioned order disappeared (see Table II). In fact, in the former case, substituents with a more negative inductive effect decrease the electron density on the ligator (oxygen atom), which causes a weakening of the hydrogen bonding to the silanol groups of silica gel, and an increased  $R_F$  value.

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