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Journal of Chromatography A, 847 (1999) 303–307

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Thin-layer chromatography of mixed tris- β -diketonato metal complexes on polyacrylonitrile sorbent

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Abstract

The effect of the composition of mixed tris- β -diketonato metal complexes on their hR_F values obtained by a thin layer of polyacrylonitrile sorbent was examined with two series of complexes of the type $[M(\text{acac})_{3-n}(\text{phacphac})_n]$ and $[M(\text{acac})_{3-n}(\text{phacphSac})_n]$, where M is Co(III), Cr(III) or Ru(III), acac=2,4-pentanedionato ion, phacphac=1,3-diphenyl-1,3-propanedionato ion and phacphSac=3-mercapto-1,3-diphenyl-prop-2-en-1-on ion ($n=0-3$). Ten mobile phases were used for their chromatographic separation. In all instances hR_F values of the examined complexes decrease when the oxygen atom in β -diketonato ligand is substituted by a less electronegative sulphur atom. It has also been established that the substitution of acac ligand results in a hR_F value decrease. In all the examined cases a linear dependence between the R_M values of the complexes and the number of acac ligands substituted by phacphSac ligands was established. The separation mechanisms and the separation factors are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Polyacrylonitrile sorbents; Metal complexes; Trisdiketonato metal complexes

1. Introduction

Polyacrylonitrile sorbent, the preparation and characteristics of which were described in our previous work [1], was applied for the separation of various classes of organic and inorganic compounds [1–6]. By examining the corresponding separation mechanisms it was shown that the sorbent in question, due to its moderate polarity and amphiphilic character, could bring about specific and nonspecific interactions with substances being separated, namely, it is favourable in both normal- and reversed-phase chromatography. In one of these works [3], the

separation mechanisms of the series of mixed complexes of $[M(\text{acac})_n(\text{phacphac})_{3-n}]$ type were examined, where M is Co(III), Cr(III) or Ru(III).

Continuing these investigations, in addition to the above mentioned complexes, an analogous series of complexes of $[M(\text{acac})_n(\text{phacphSac})_{3-n}]$ type were chromatographed in this work. When studying the chromatographic behaviour of these two series of complexes, we intended, in the first place, to examine the effect of the electronegativity of the ligator atoms on the retention of the transition metal complexes on polyacrylonitrile sorbent (PANS). Namely, such an effect has been so far examined in detail only under TLC conditions on silica gel by using some weakly polar mobile phases [7]. It was established that the hR_F values of the complexes increase

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when oxygen atom of β -diketonato ligand was substituted by a less electronegative sulphur atom.

2. Experimental

2.1. Syntheses

All ligands and complexes were prepared according to the earlier described procedures cited in Table 1.

2.2. Chromatography

Chromatographic separations were carried out by horizontal thin-layer chromatography on polyacrylonitrile plates (10×10 cm). For this purpose a Camag HPTLC horizontal developing chamber under the tank configuration developing conditions was used. The polyacrylonitrile sorbent was developed recently in our laboratory [1]. Its application to plates was performed as already have been described

[1]. Standard solutions (about 2 mg/cm³) of the investigated complexes were prepared in chloroform; plates were spotted with 0.2 μ l aliquots of freshly prepared solutions. Before development the spotted plates were equilibrated for 30 min in a chromatographic chamber saturated with vapour of the mobile phases being used. All solvents were of analytical grade. The compositions of the mobile phases used are given in Table 2. After development, the spots of individual complexes were visible owing to their natural colours.

3. Results and discussion

The examination of the effect of the composition of mixed tris- β -diketonato metal complexes on their hR_F values by TLC was carried out chromatographically on 21 Co(III), Cr(III) and Ru(III) complexes which were classified in three series according to the transition metal. Ten non-aqueous mobile phases were used for their separation, two monocomponent

Table 1
 hR_F values of investigated complexes

No.	Complex ^a	Ref. for synth.	hR_F ^b									
			1	2	3	4	5	6	7	8	9	10
1	[Co(acac) ₃]	[8]	94	24	62	76	57	42	45	58	86	78
2	[Co(acac) ₂ (phacphac)]	[8,9]	84	21	51	70	49	36	35	49	79	66
3	[Co(acac) ₂ (phacphSac)]	[10]	62	9	36	65	43	29	16	30	61	56
4	[Co(acac)(phacphac) ₂]	[8,9]	73	17	41	62	39	24	23	31	67	44
5	[Co(acac)(phacphSac) ₂]	[10]	42	7	25	58	29	20	13	26	44	39
6	[Co(phacphac) ₃]	[8,9]	44	13	20	53	33	11	13	15	40	32
7	[Co(phacphSac) ₃]	[10,11]	25	4	16	46	21	9	5	13	33	30
8	[Cr(acac) ₃]	[12]	96	45	70	68	69	61	57	69	90	78
9	[Cr(acac) ₂ (phacphac)]	[9,12]	88	19	42	59	59	31	29	44	67	50
10	[Cr(acac) ₂ (phacphSac)]	[9,12]	58	11	33	47	41	15	14	25	57	47
11	[Cr(acac)(phacphac) ₂]	[9]	65	14	33	50	43	17	17	31	55	40
12	[Cr(acac)(phacphSac) ₂]	[6]	53	10	22	45	37	11	11	19	45	36
13	[Cr(phacphac) ₃]	[11]	50	8	17	45	31	11	8	21	31	29
14	[Cr(phacphSac) ₃]	[13]	34	7	10	39	29	4	6	11	29	25
15	[Ru(acac) ₃]	[14]	95	19	64	77	66	47	28	49	80	78
16	[Ru(acac) ₂ (phacphac)]	[9,14]	85	10	42	72	54	20	14	44	65	58
17	[Ru(acac) ₂ (phacphSac)]	[9,14]	81	8	37	70	47	17	12	29	61	55
18	[Ru(acac)(phacphac) ₂]	[9,14]	65	6	30	61	43	17	8	22	47	44
19	[Ru(acac)(phacphSac) ₂]	[9]	54	5	28	54	37	6	7	15	33	39
20	[Ru(phacphac) ₃]	[9,14]	40	4	19	56	35	6	6	20	25	31
21	[Ru(phacphSac) ₃]	[15]	36	3	14	47	29	1	3	8	20	22

^a acac=2,4-pentanedionato ion; phacphac=1,3-diphenyl-1,3-propanedionato ion; phacphSac=3-mercapto-1,3-diphenyl-prop-2-en-1-one ion; $n=0-3$.

^b The composition of the mobile phases are given in Table 2.

Table 2
Mobile phases used

No.	Composition	Proportions (v/v)	Polarity (P) ^[6]
1	<i>n</i> -Octanol	–	3.2
2	Cyclohexane	–	0.0
3	<i>n</i> -Hexane–dichloromethane	80:20	0.74
4	<i>n</i> -Hexane–dioxane	90:10	0.48
5	Cyclohexane–acetone	95:5	0.27
6	<i>n</i> -Hexane–diethyl ether	70:30	0.30
7	<i>n</i> -Hexane–carbon tetrachloride	75:25	0.425
8	<i>n</i> -Hexane–benzene	80:20	0.6
9	Acetone–water	70:30	6.48
10	Tetrahydrofuran–water	60:40	6.12

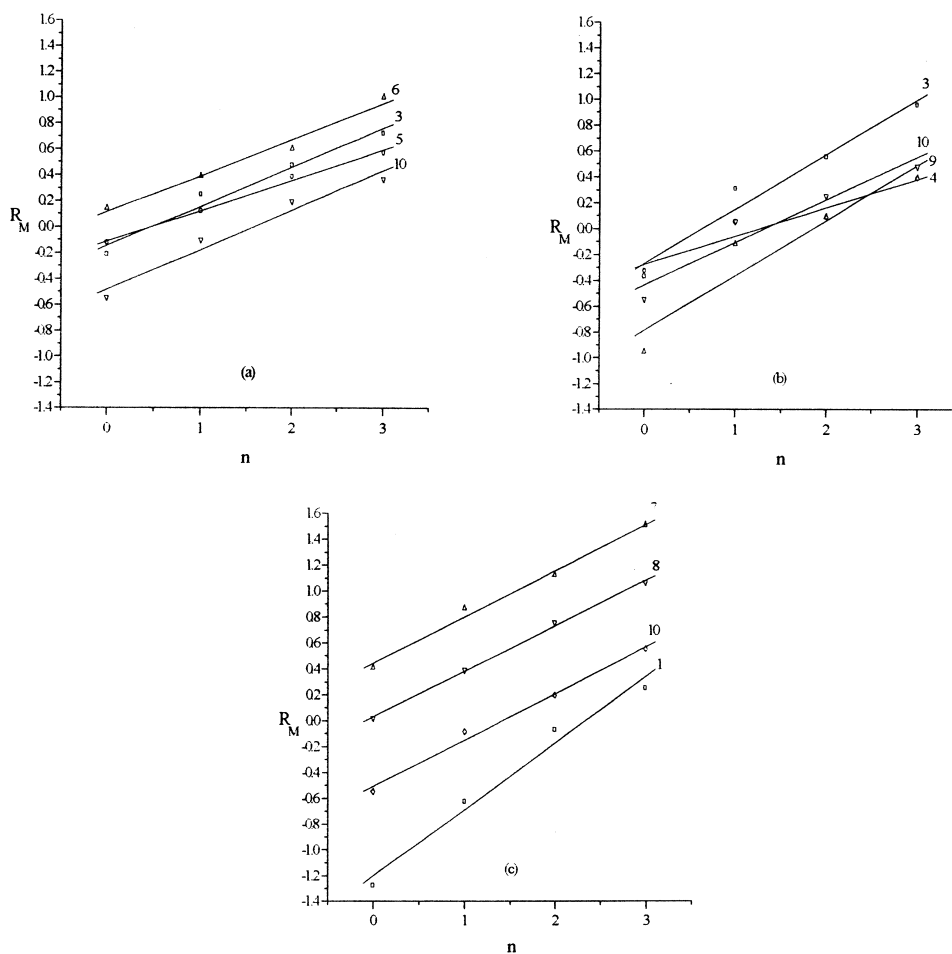


Fig. 1. Dependence of R_M values on the number of 2,4-pentanedionato ligands (acac) substituted by 3-mercapto-1,3-diphenyl-prop-2-en-1-one ligands (phacphSac) in the $[M(acac)_{3-n}(phacphSac)_n]$ -type complexes ($n=0-3$). (a) Cobalt(III); (b) chromium(III); (c) ruthenium(III). The numbers on the lines refer to the mobile phases used (see Table 2).

and six binary mobile phases, as well as two aqueous mobile phases (Table 2). The hR_F values obtained are shown in Table 1.

On the basis of the obtained results, in all the examined cases it has been established that the substitution of acac ligand either by phacphac or by phacphSac ligands leads to the retention increase of the corresponding complexes. In addition, by comparison of hR_F values of the analogous complexes of $[M(\text{acac})_{3-n}(\text{phacphac})_n]$ type and $[M(\text{acac})_{3-n}(\text{phacphSac})_n]$, it is seen that, regardless of the mobile phases composition used, the substitution of the ligator oxygen atom in dibenzoylmethanato ligand by a less electronegative sulphur atom leads to a stronger sorption.

Such a chromatographic behaviour of the complexes examined is contrary to the results obtained on a silica gel thin layer [7], where the adsorption of hydrogen bonds between the ligator atoms in the complex and the silanol groups of the sorbent was proposed as a predominant separation mechanism for these compounds.

However, the obtained results are in agreement with the previously established chromatographic behaviour of the complexes of $[M(\text{acac})_{3-n}(\text{phacphac})_n]$ type on the PANS thin layer [3]. Accordingly, the fact that by using the nonaqueous mobile phases (normal-phase chromatography), the hR_F values of both series of the examined complexes decrease with an increase in phenyl-group number in their molecules, could be explained by the earlier

described [3] donor–acceptor interactions between the π -electron systems of the corresponding β -diketonato ligands and the PANS cyano groups. In the case of aqueous mobile phases (reversed-phase chromatography), in addition to this kind of interactions, the same sequence of the hR_F values of the examined complexes is also caused by the nonspecific hydrophobic interactions between the hydrocarbon chains of a sorbent and the nonpolar parts of β -diketonato ligands. The fact that the substituted ligator oxygen atoms by less electronegative sulphur atoms in all the examined cases leads to a decrease in hR_F values of the corresponding complexes supports the hypothesis on donor–acceptor interactions as a predominant mechanism for the above chromatographic separations. Specifically, due to the less electronegative sulphur atoms in the complexes of $[M(\text{acac})_{3-n}(\text{phacphSac})_n]$ type, the electron delocalisation of π -conjugated systems is less pronounced in relation to the analogous complexes of $[M(\text{acac})_{3-n}(\text{phacphac})_n]$ type. Therefore, it could be assumed that in the monothio series of complexes the electronic density at the aromatic rings of ligands is to some extent greater, thus accounting for their stronger interactions with cyano groups of the sorbent, i.e., the stronger retention.

The expected linear dependence [3,7,9] between R_M values of complexes and the number of acac ligands substituted by phacphSac ligands was observed. Some of these straight lines are shown in Fig. 1.

Table 3

The separation factors of adjacent members of the investigated series of complexes

Solvent ^a	$[M(\text{acac})_{3-n}(\text{phacphac})_n]$ ^b			$[M(\text{acac})_{3-n}(\text{phacphSac})_n]$ ^c		
	Co(III)	Cr(III)	Ru(III)	Co(III)	Cr(III)	Ru(III)
1	2.62	2.98	3.05	3.44	3.23	3.27
2	1.28	2.03	1.77	1.88	2.06	1.93
3	1.83	2.16	1.94	2.01	2.64	2.13
4	1.41	1.38	1.41	1.63	1.65	1.60
5	1.40	1.72	1.53	1.72	1.69	1.66
6	1.86	2.32	2.30	1.91	3.08	4.30
7	1.77	2.43	1.83	2.33	2.55	2.27
8	1.98	2.00	1.66	1.99	2.47	2.24
9	2.38	2.58	2.27	2.28	2.65	2.58
10	2.00	1.99	1.97	2.02	2.13	2.28

^a The compositions of the mobile phases are given in the Table 2.

^b acac=2,4-pentanedionato ion; phacphac=1,3-diphenyl-1,3-propanedionato ion; $n=0-3$.

^c phacphSac=3-mercapto-1,3-diphenyl-prop-2-en-1-one ion.

Table 4

The separation factors of pairs of the investigated analogous complexes of type $[M(acac)_{3-n}(phacphac)_n]$ and $[M(acac)_{3-n}(phacphSac)_n]$ ^a

Solvent ^b	Co(III): <i>n</i>			Cr(III): <i>n</i>			Ru(III): <i>n</i>		
	1	2	3	1	2	3	1	2	3
1	2.01	2.64	3.47	1.94	212	2.30	1.21	1.30	1.39
2	1.87	2.74	4.02	1.32	1.35	1.37	1.15	1.26	1.37
3	1.43	1.57	1.72	1.33	1.63	2.00	1.12	1.24	1.37
4	1.30	1.50	1.72	1.29	1.54	1.85	1.13	1.28	1.46
5	1.25	1.53	1.89	1.32	1.30	1.27	1.17	1.27	1.38
6	1.17	1.20	1.23	1.63	2.17	2.87	1.54	2.88	5.41
7	1.74	2.30	3.04	1.50	1.58	1.66	1.17	1.44	1.79
8	1.31	1.32	1.33	1.59	1.96	2.42	1.49	2.00	2.70
9	1.22	1.17	1.12	1.24	1.28	1.31	1.22	1.39	1.58
10	1.19	1.20	1.21	1.10	1.17	1.25	1.13	1.31	1.52

^a acac=2,4-pentanedionato ion; phacphac=1,3-diphenyl-1,3-propanedionato ion; phacphSac=3-mercapto-1,3-diphenyl-prop-2-en-1-one ion; *n*=0–3.

^b The compositions of the mobile phases are given in the Table 2.

In Table 3 the separation factors of the adjacent members of the series of complexes of types $[M(acac)_{3-n}(phacphac)_n]$ and $[M(acac)_{3-n}(phacphSac)_n]$ (*n*=0–3) are listed, which were calculated in the previously described way [6,7,17]. As seen from Table 3, the separation factors of the second type of series of complexes are always greater. Since the first member of both series is the same complex, $[M(acac)_3]$, this is in accordance with the above established fact that complexes containing a less electronegative sulphur atom as a ligator atom have lower hR_F values.

Finally, in Table 4 the separation factors of the analogous complexes of $[M(acac)_{3-n}(phacphac)_n]$ type and of $[M(acac)_{3-n}(phacphSac)_n]$ type, (*n*=0–3) are given. From the results obtained it is seen that an increase in the value of *n* leads to an increase in separation factors. This is also in accordance with our previous results [7] because with an increase in *n* values in analogous pairs the number of less electronegative sulphur atoms increases, which results in their better separation.

Acknowledgements

The authors are grateful to the Serbian Research Fund for financial support.

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