Journal of Chromatography, 547 (1991) 225–237
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 232

Reversed-phase liquid chromatographic retention of geometrical isomers of tris(β-diketonato)–chromium(III) and tris(β-diketonato)–cobalt(III)

Comparison with liquid–liquid partition in a dodecane–(methanol–water) system

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(Received December 27th, 1990)

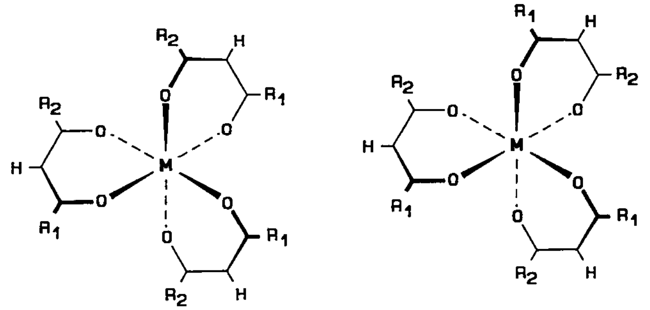
ABSTRACT

The retention of the *fac* and *mer* isomers of chromium(III) and cobalt(III) complexes with eight asymmetrical β-diketones in the octadecyl-bonded silica (ODS)–(methanol–water) system was studied. The retention order for two geometrical isomers depends on the structure of the complexing β-diketone; the retention order, *fac* < *mer*, is found for complexes of the β-diketones which possess a fluorinated functional group in each molecule, whereas the reverse order is found for complexes of β-diketones without a fluorinated moiety. The capacity factors (k') of the chromium(III) complex isomers were compared with their partition coefficients (P) between dodecane and methanol–water of an identical composition to the mobile phase used in the chromatographic separation. It was found that the transfer of a complex from a methanol–water phase occurs more easily to ODS than to dodecane. The retention sequence for the *fac* and *mer* isomers of each metal complex is the same as the increasing order of P values. The difference in k' between the *mer* and *fac* isomers is smaller than the difference in the P value.

INTRODUCTION

Metal β-diketonates have been studied intensively in gas, column liquid and thin-layer chromatography as well as in solvent extraction procedures. The first application of high-performance liquid chromatography (HPLC) to the separation of metal–β-diketonato complexes was reported by Huber *et al.* in 1972 [1]. Since that time, many papers dealing with the HPLC separation of various metal–β-diketonate complexes have been published [2–7], whereas the HPLC of the geometrical isomers of β-diketonato complexes has only rarely been described.

The octahedral complex of a trivalent metal coordinated with three molecules of an asymmetrical β-diketone possesses two geometrical isomers, with meridional (*mer*) and facial (*fac*) configurations about an octahedral coordination sphere, as illustrated in Fig. 1. Fay and Piper separated the *fac* and *mer* forms of benzoylacet-



mer form

fac form

Fig. 1. Configurations of the geometrical isomers of a tris(β-diketonato) complex of a trivalent metal.

onates (1-phenyl-1,3-butanedionates) [8] and trifluoroacetylacetonates (1,1,1-trifluoro-2,4-pentanedionates) [9] of chromium(III), cobalt(III) and rhodium(III) by traditional adsorption chromatography with aluminium oxide. The successful HPLC separation of the geometrical isomers of chromium(III) and cobalt(III) complexes of asymmetrical β-diketones were carried out using a silica gel column [10] and a phenyl-bonded silica gel column [11]. The adsorption characteristics of the isomers of several chromium(III) β-diketonates on silica gel have also been reported [12]. In all these examples of chromatography with the combination of a polar stationary phase and a less polar mobile phase, the *fac* form showed a larger retention than the *mer* form with different metal β-diketonates.

The retention order, *fac* < *mer*, was reported for the chromium(III) complexes of trifluoroacetylacetone and also of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, in the case of the reversed-phase HPLC with an alkyl-bonded silica gel [13].

This paper reports an investigation of the retention sequence of the *fac* and *mer* isomers of octahedral metal complexes of β-diketones in reversed-phase HPLC. Chemically inert chromium(III) and cobalt(III) complexes with eight asymmetrical β-diketones were taken as model complexes. To clarify the retention characteristics and selectivity for the *mer* and *fac* isomers on an octadecyl-bonded phase, the chromatographic retention was compared with liquid–liquid partition using dodecane as a non-polar phase. The reversed-phase chromatographic retention of several chromium(III) complexes with symmetrical β-diketones in the ODS–(methanol–water) system was previously compared with the partition coefficient in the dodecane–(methanol–water) system [7].

EXPERIMENTAL

Materials

The tris(β-diketonato) complexes of chromium(III) and cobalt(III) listed in Table I were prepared by modifying the methods reported for tris(acetylacetonato)–chromium(III) [14] and tris(acetylacetonato)–cobalt(III) [15], respectively. Prior to the preparation of these metal complexes, the β-diketones which were not commer-

TABLE I

β-DIKETONATO COMPLEXES INVESTIGATED

Complex [a]	R_1 [b]	R_2 [b]	Abbreviation	Graph symbol
Tris(acetylacetonato)-chromium(III)	CH_3	CH_3	$Cr(acac)_3$	○
Tris(propionylacetonato)-chromium(III)	CH_3	C_2H_5	$Cr(prac)_3$	●
Tris(butyrylacetonato)-chromium(III)	CH_3	C_3H_7	$Cr(buac)_3$	□
Tris(valerylacetonato)-chromium(III)	CH_3	C_4H_9	$Cr(vac)_3$	■
Tris(hexanoylacetonato)-chromium(III)	CH_3	C_5H_{11}	$Cr(hac)_3$	△
Tris(benzoylacetonato)-chromium(III)	CH_3	C_6H_5	$Cr(bzac)_3$	▲
Tris(trifluoroacetylacetonato)-chromium(III)	CF_3	CH_3	$Cr(tfa)_3$	▽
Tris(pivaroyltrifluoroacetonato)-chromium(III)	CF_3	$C(CH_3)_3$	$Cr(pfa)_3$	◑
Tris(benzoyltrifluoroacetonato)-chromium(III)	CF_3	C_6H_5	$Cr(bzfa)_3$	▼
Tris(acetylacetonato)-cobalt(III)	CH_3	CH_3	$Co(acac)_3$	○
Tris(propionylacetonato)-cobalt(III)	CH_3	C_2H_5	$Co(prac)_3$	●
Tris(butyrylacetonato)-cobalt(III)	CH_3	C_3H_7	$Co(buac)_3$	□
Tris(valerylacetonato)-cobalt(III)	CH_3	C_4H_9	$Co(vac)_3$	■
Tris(hexanoylacetonato)-cobalt(III)	CH_3	C_5H_{11}	$Co(hac)_3$	△
Tris(benzoylacetonato)-cobalt(III)	CH_3	C_6H_5	$Co(bzac)_3$	▲
Tris(trifluoroacetylacetonato)-cobalt(III)	CF_3	CH_3	$Co(tfa)_3$	▽
Tris(pivaroyltrifluoroacetonato)-cobalt(III)	CF_3	$C(CH_3)_3$	$Co(pfa)_3$	◑
Tris(benzoyltrifluoroacetonato)-cobalt(III)	CF_3	C_6H_5	$Co(bzfa)_3$	▼

[a] Geometrical isomers are not distinguished.
[b] See Fig. 1.

cially available (Hbzac, Htfa, Hbzfa and Hpfa were obtained from Wako, Osaka, or Dojin Labs., Kumamoto, Japan) were synthesized by the literature method [16].

Geometrical isomers of each metal β-diketonate were resolved by silica gel column chromatography with hexane–benzene or benzene–ethyl acetate, as shown in Table II. In the case of the cobalt(III) complexes, the early and late eluted species

TABLE II

PREPARATIVE SEPARATION OF GEOMETRICAL ISOMERS OF METAL β-DIKETONATO COMPLEXES

Complex	Column	Eluent [a]
$Cr(prac)_3$, $Co(prac)_3$ $Cr(bzac)_3$, $Co(bzac)_3$	LiChroprep Si60 [b] (25 cm × 2.5 cm)	Bz–EtOAc (100:5, v/v)
$Cr(buac)_3$, $Co(buac)_3$ $Cr(vac)_3$, $Co(vac)_3$	Wakogel C-300 [c] (5 cm × 2.5 cm)	Bz–EtOAc (100:4, v/v)
$Cr(hac)_3$, $Co(hac)_3$	Wakogel C-300 (4 cm × 2.5 cm)	Bz–EtOAc (100:3, v/v)
$Cr(tfa)_3$, $Co(tfa)_3$	Wakogel C-300 (10 cm × 2.5 cm)	Bz–hexane (40:60, v/v)
$Cr(bzfa)_3$, $Co(bzfa)_3$	Wakogel C-300 (15 cm × 2.5 cm)	Bz–hexane (40:60, v/v)
$Cr(pfa)_3$, $Co(pfa)_3$	Wakogel C-300 (5 cm × 2.5 cm)	Bz–hexane (10:90, v/v)

[a] Bz = Benzene; EtOAc = ethyl acetate.
[b] 40–63 μm, Merck, Darmstadt, Germany.
[c] 300 mesh; Wako, Osaka, Japan.

from the column were identified as *mer* and *fac* forms by comparing their ^{1}H-NMR spectra [8,9,17]. However, for the paramagnetic chromium(III) complexes to which ^{1}H-NMR could not be applied, the *mer* and *fac* forms were regarded as the early and late eluted fractions from the column, respectively, by reference to the elution sequence of the geometrical isomers of cobalt(III) complexes. In each instance, the yield of the *mer* form was about three to five times the yield of the *fac* form (the ratio of the statistical yields of the *mer* form to the *fac* form is 3:1).

Dodecane was distilled under reduced pressure after stirring with an equivolume mixture of fumic and concentrated sulphuric acids for 1 day. The water was doubly-distilled. Other chemicals were of analytical-reagent grade.

Equipment

A Hitachi Model 655-15 pump (Tokyo, Japan), a Rheodyne 7125 sample injection valve with a 10-μl sample loop (Cotani, CA, USA), a Shimadzu SPD-6AV UV–visible absorption detector and a C-R1A chromatographic data processor (Kyoto, Japan) were assembled into an HPLC system.

High-performance liquid chromatography

A column packed with octadecyl-bonded silica gel (TSK-Gel ODS-120T; particle size 5 μm, 15 cm × 4.6 mm I.D.; Tosoh, Tokyo, Japan) was used. The methanol–water used as the mobile phase was prepared by weighing. A sample solution of each metal complex was prepared at a concentration of about $1 \cdot 10^{-4}$ *M* in methanol, and a 1- μl aliquot of the solution was injected on to the column. The detection wavelength was set at 254 nm. The temperature was 25 ± 1°C.

Liquid–liquid partition

Aliquots (1 ml) of both dodecane and methanol–water (both of these liquids contained a metal complex at the $1 \cdot 10^{-3}$ *M* level) were agitated in a glass tube at 300 strokes per min for 30 min. After the completion of phase separation by centrifuging, a 10-μl portion of each liquid phase was injected into a reversed-phase HPLC column (5 μm Inertsil ODS, 150 mm × 4.6 mm I.D.; Gasukuro Kogyo, Tokyo, Japan) which used an appropriate methanol–water binary mobile phase for the elution of the metal complex within a few minutes. The partition coefficient was calculated as a ratio of the chromatographic peak areas measured for the metal complex in the dodecane phase to the methanol–water phase [18]. All these experiments were carried out in a thermostated room at 25 ± 1°C.

RESULTS AND DISCUSSION

Capacity factors

Every metal β-diketonato complex gave a sharp and symmetrical chromatographic peak, which implied the absence of undesirable adsorption and chemical changes, such as demetallation and isomerization, of the complex during the chromatographic process.

Prior to the calculation of the capacity factor (k') of each metal complex from its retention volume, the column void volume was determined using sodium nitrate as an unretained compound by the column. The k' values of tris(β-diketonato)–chromium(III) and –cobalt(III) were determined with a relative standard deviation of less than 1% ($n=3$), with all compositions of methanol–water used [the range of the molar fraction of methanol (X_{CH_3OH}) in the binary mixture was 0.5–1.0]. The k' values are summarized in Table III. The k' value of the chromium(III) complexes are larger than those of the cobalt(III) complexes in most instances.

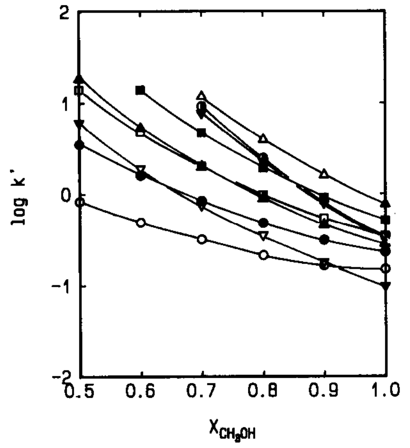
Figs. 2 and 3 show the variation of the retention of the chromium(III) and cobalt(III) complexes with the molar fraction of methanol in the mobile phase, respectively. The plots are restricted to the *mer* isomers of the complexes to avoid complicated illustration [no geometrical isomer is present for $Cr(acac)_3$ and Co-

TABLE III

CAPACITY FACTORS OF CHROMIUM(III) AND COBALT(III) β-DIKETONATES ON TSK-GEL ODS-120T WITH METHANOL–WATER AT 25.0°C

Complex	X_{CH_3OH} [a]					
	0.50	0.60	0.70	0.80	0.90	1.00
$Cr(acac)_3$	0.83	0.49	0.32	0.21	0.17	0.15
mer-$Cr(prac)_3$	3.47	1.59	0.84	0.48	0.31	0.23
fac-$Cr(prac)_3$	3.79	1.69	0.88	0.50	0.32	0.24
mer-$Cr(buac)_3$	13.9	4.76	2.00	0.97	0.54	0.35
fac-$Cr(buac)_3$	16.1	5.33	2.19	1.05	0.57	0.37
mer-$Cr(vac)_3$		13.9	4.70	1.91	0.91	0.52
fac-$Cr(vac)_3$		16.2	5.33	2.12	0.99	0.55
mer-$Cr(hac)_3$			11.8	3.94	1.60	0.78
fac-$Cr(hac)_3$			13.4	4.37	1.74	0.83
mer-$Cr(bzac)_3$	18.5	5.30	1.99	0.90	0.46	0.29
fac-$Cr(bzac)_3$	22.2	6.10	2.21	0.97	0.49	0.30
mer-$Cr(tfa)_3$	6.07	1.87	0.75	0.36	0.18	0.10
fac-$Cr(tfa)_3$	5.56	1.72	0.69	0.33	0.16	0.09
mer-$Cr(pfa)_3$			9.23	2.46	0.84	0.34
fac-$Cr(pfa)_3$			7.69	2.14	0.76	0.32
mer-$Cr(bzfa)_3$			7.73	2.25	0.80	0.34
fac-$Cr(bzfa)_3$			5.46	1.64	0.60	0.27
$Co(acac)_3$	0.72	0.44	0.30	0.21	0.17	0.16
mer-$Co(prac)_3$	2.89	1.39	0.77	0.46	0.31	0.24
fac-$Co(prac)_3$	3.13	1.48	0.81	0.48	0.32	0.25
mer-$Co(buac)_3$	11.5	4.13	1.83	0.93	0.54	0.36
fac-$Co(buac)_3$	13.0	4.56	1.97	0.98	0.56	0.37
mer-$Co(vac)_3$		12.0	4.24	1.79	0.89	0.52
fac-$Co(vac)_3$		13.8	4.76	1.97	0.96	0.55
mer-$Co(hac)_3$			10.6	3.68	1.56	0.78
fac-$Co(hac)_3$			11.8	4.03	1.67	0.83
mer-$Co(bzac)_3$	14.5	4.40	1.73	0.82	0.44	0.28
fac-$Co(bzac)_3$	17.8	5.14	1.94	0.88	0.47	0.29
mer-$Co(tfa)_3$	5.35	1.73	0.71	0.32	0.15	0.10
fac-$Co(tfa)_3$	5.03	1.61	0.65	0.29	0.14	0.09
mer-$Co(pfa)_3$			9.26	2.56	0.88	0.37
fac-$Co(pfa)_3$			7.62	2.21	0.79	0.35
mer-$Co(bzfa)_3$			7.06	2.13	0.78	0.34
fac-$Co(bzfa)_3$			4.99	1.56	0.59	0.27

[a] X_{CH_3OH} = molar fraction of methanol in the mobile phase.



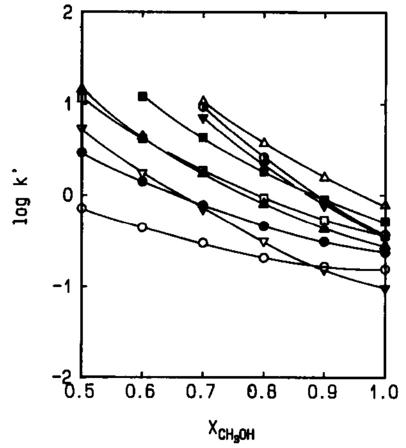


Fig. 2. Variation of the retention (log k') of tris(β-diketonato)–chromium(III) with the molar fraction of methanol (X_{CH_3OH}) in the methanol–water binary mobile phase. Symbols refer to the chromium(III) complexes as given in Table I.

Fig. 3. Variation of the retention of tris(β-diketonato)–cobalt(III) with the molar fraction of methanol (X_{CH_3OH}) in the mobile phase. Symbols refer to the cobalt(III) complexes as given in Table I.

(acac)3]. The general shapes of the log k' *versus* X_{CH_3OH} curves for the chromium(III) and cobalt(III) complexes of a particular β-diketone are similar; the k' value of each metal complex decreases with increasing X_{CH_3OH}. This does not disagree with the general retention trends observed so far with many kinds of non-electrolytes in reversed-phase HPLC.

The metal complexes are classified into the following two groups with respect to the dependence of their retention on the composition of the mobile phase: (1) the complexes of the β-diketones possessing a trifluoromethyl group (fluorinated β-diketones); and (2) those of other β-diketones (non-fluorinated β-diketones). The methanol content of the mobile phase affected the retention more significantly for the complexes of fluorinated β-diketones than for the non-fluorinated compounds. Accordingly, the log k' *versus* X_{CH_3OH} plots for the complexes of these two types of β-diketones cross each other (Fig. 2 and Fig. 3). The retention order of the complexes of the fluorinated or non-fluorinated series of β-diketones was not altered by a change in the mobile phase composition; the capacity factors of both chromium(III) and cobalt(III) complexes increased in the following order of complexing β-diketones: acac < prac < buac < bzac ≈ vac < hac, in the series of non-fluorinated β-diketones, and tfa < bzfa < pfa, in the series of fluorinated compounds. It was found that for the complexes of alkyl substituted β-diketones the retention increases with increasing number of carbon atoms in the alkyl moiety of the β-diketone.

Retention difference between geometrical isomers

The *fac* forms of both the chromium(III) and cobalt(III) complexes of a fluorinated β-diketone always eluted earlier than the *mer* forms of the corresponding complexes, whereas a reversed elution sequence was always observed for the complexes of non-fluorinated β-diketone. Typical chromatograms showing these two types of

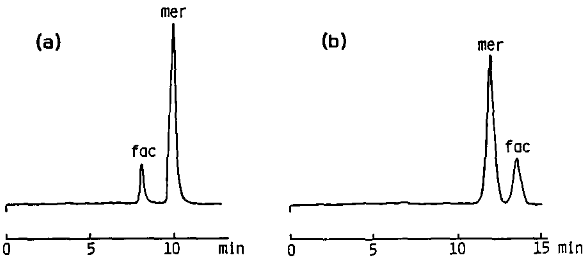
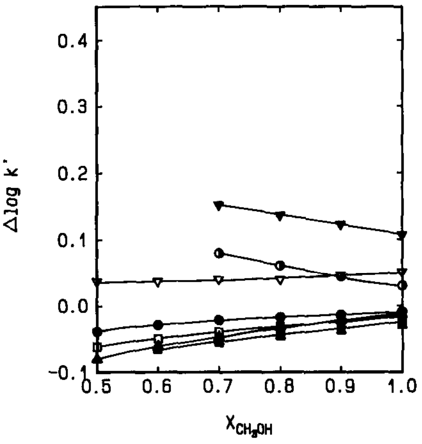


Fig. 4. High-performance liquid chromatographic separation of geometrical isomers of (a) $Cr(bzfa)_3$ and (b) $Cr(bzac)_3$. Column: TSK-gel ODS-120T, 5 μm, 150 mm × 4.6 mm I.D. Mobile phase: (a) X_{CH_3OH} = 0.8, 0.50 ml/min; (b) X_{CH_3OH} = 0.6, 0.80 ml/min.

elution sequences in the separation of the geometrical isomers studied here are illustrated in Fig. 4. A similar effect of the structure of β-diketone on the elution sequence of the geometrical isomers of its metal complex was not observed with a silica gel column from which the *fac* form always eluted later than the *mer* form, regardless of the functional groups possessed by the β-diketone.

The retention difference between the *mer* and *fac* forms of the chromium(III) and cobalt(III) complexes observed in the reversed-phase separation mode used are plotted as a function of X_{CH_3OH} of the mobile phase in Figs. 5 and 6, respectively, where

$$\Delta \log k' = \log k'_{mer} - \log k'_{fac} \quad (1)$$



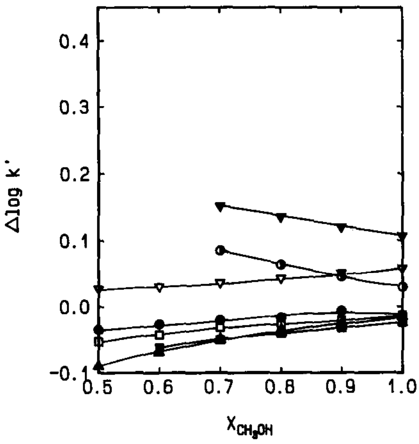


Fig. 5. Effect of the composition of the methanol–water mobile phase on the Δlog k' value for geometrical isomers of tris(β-diketonato)-chromium(III). Symbols refer to the chromium(III) complexes as given in Table I.

Fig. 6. Effect of the mobile phase composition on the Δlog k' value for geometrical isomers of tris(β-diketonato)–cobalt(III). Symbols refer to the cobalt(III) complexes as given in Table I.

TABLE IV

PARTITION COEFFICIENT (P) OF TRIS(β-DIKETONATO)–CHROMIUM(III) IN THE DODECANE–(METHANOL–WATER) SYSTEM AT 25.0°C

Complex	X_{CH_3OH}[b]	$(P \times 10^2)$[a]		
	0.40	0.60	0.80	1.00
Cr(acac)$_3$	3.28 ± 0.05	1.86 ± 0.04	1.64 ± 0.05	2.20 ± 0.03
mer-Cr(prac)$_3$		15.1 ± 0.4	7.96 ± 0.23	7.68 ± 0.24
fac-Cr(prac)$_3$		16.2 ± 0.3	8.32 ± 0.29	8.17 ± 0.17
mer-Cr(buac)$_3$		80.8 ± 1.1	25.7 ± 0.2	16.0 ± 0.5
fac-Cr(buac)$_3$		82.9 ± 0.4	26.8 ± 0.3	16.9 ± 0.7
mer-Cr(vac)$_3$		322 ± 2	67.9 ± 0.1	28.2 ± 0.4
fac-Cr(vac)$_3$		329 ± 4	70.5 ± 0.4	29.9 ± 0.3
mer-Cr(hac)$_3$		1410 ± 40	195 ± 4	54.4 ± 0.4
fac-Cr(hac)$_3$		1240 ± 20	191 ± 4	55.2 ± 0.6
mer-Cr(bzac)$_3$	781 ± 12	67.6 ± 0.5	15.2 ± 0.3	7.20 ± 0.13
fac-Cr(bzac)$_3$	824 ± 18	74.1 ± 1.0	16.6 ± 0.2	7.73 ± 0.09
mer-Cr(tfa)$_3$	524 ± 9	36.5 ± 0.5	6.07 ± 0.11	1.84 ± 0.06
fac-Cr(tfa)$_3$	375 ± 7	26.6 ± 0.4	4.58 ± 0.02	1.44 ± 0.02
mer-Cr(pfa)$_3$		4810 ± 70	283 ± 1	32.3 ± 0.5
fac-Cr(pfa)$_3$		2660 ± 20	161 ± 1	19.1 ± 0.5
mer-Cr(bzfa)$_3$		1970 ± 20	119 ± 0	14.1 ± 0.2
fac-Cr(bzfa)$_3$		809 ± 22	47.1 ± 0.7	6.05 ± 0.11

[a] Mean ± standard deviation ($n = 3$).

[b] X_{CH_3OH} = molar fraction of methanol in the methanol–water phase.

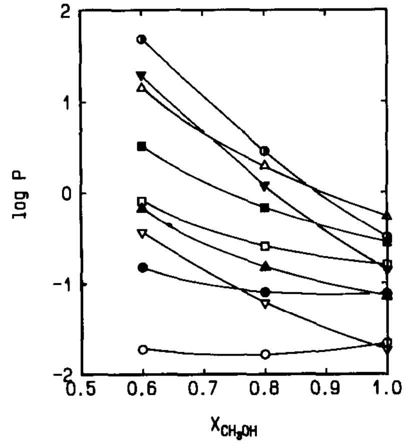
The $\Delta \log k'$ corresponds to the logarithmic separation factor between the isomers [= $\log (k'_{mer}/k'_{fac})$].

The magnitudes of $\Delta \log k'$ for the complexes of fluorinated β-diketones are positive regardless of the composition of methanol–water mobile phase, whereas those for the complexes of non-fluorinated β-diketones are always negative.

Liquid–liquid partition coefficients

The liquid–liquid partition coefficients (P) of the chromium(III) complexes were determined using dodecane and methanol–water as the non-polar and the polar liquid phases, respectively. P was defined as the concentration ratio of a metal complex in the non-polar to that in the polar liquid phase. The results are summarized in Table IV. The P value of each complex decreased with an increase in the methanol content of the polar liquid phase, although a slight reverese trend was found, particularly for the complexes of acac and prac when the composition of the polar phase approached pure methanol. The influence of the methanol–water composition on the partition coefficient was more significant for a complex of a fluorinated β-diketone than for that of non-fluorinated compound, so that, in some instances, the log P *versus* X_{CH_3OH} plots for the complexes of such different types of β-diketones cross each other, as shown in Fig. 7 (where the plots for *mer* forms are given in order for simplification of the illustration).

The difference in the partition coefficient between the *mer* form (P_{mer}) and *fac*



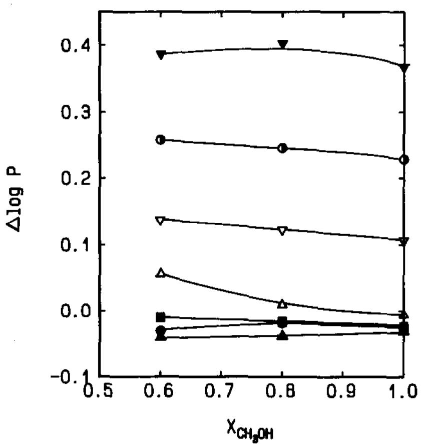


Fig. 7. Variation of the partition coefficient (P) of tris(β-diketonato)-chromium(III) with the methanol content of the mobile phase. Symbols refer to the chromium(III) complexes as given in Table I.

Fig. 8. Effect of the methanol content of the mobile phase on the $\Delta\log P$ value for geometrical isomers of tris(β-diketonato)-chromium(III) complexes. Symbols refer to the chromium(III) complexes as given in Table I.

form (P_{fac}) of each chromium(III) complex is plotted as a function of X_{CH_3OH} in the polar liquid phase in Fig. 8, where $\Delta\log P$ is defined as

$$\Delta\log P = \log P_{mer} - \log P_{fac} \qquad (2)$$

The $\Delta\log P$ corresponds to the logarithmic separation factor between the isomers [log (P_{mer}/P_{fac})]. It is seen in Fig. 8 that the $\Delta\log P$ values of the complexes of fluorinated β-diketones such as tfa, pfa and bzfa are positive, regardless of X_{CH_3OH}, whereas those of non-fluorinated β-diketones are slightly negative, except for $Cr(hac)_3$ under certain conditions of X_{CH_3OH}.

Comparison of the liquid chromatographic retention with the liquid–liquid partition coefficient

Comparing Fig. 7 with both Figs. 2 and 3, it is found that the liquid–liquid partition of each metal complex in the dodecane–(methanol–water) system is similar to the chromatographic retention with respect to their dependence on the composition of the methanol–water mixture.

The capacity factor, k', in these liquid chromatography studies, is a combined function of the distribution coefficient (K), defined as a concentration ratio of a metal complex in the stationary phase to the mobile phase, and the volume ratio (φ) of these phases, represented by

$$\log k' = \log K + \log \varphi \qquad (3)$$

If the partition in the dodecane–(methanol–water) system is almost equivalent to the distribution in the ODS–(methanol–water) system, K is close to P, provided that the

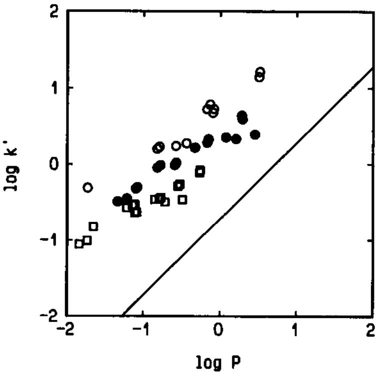


Fig. 9. Chromatographic capacity factor (log k') of tris(β-diketonato)–chromium(III) plotted against the liquid–liquid partition coefficient (log P) in the dodecane–(methanol–water) system. X_{CH_3OH}: ○ = 0.6; ● = 0.8; □ = 1.0.

methanol–water mixtures used in both systems are of identical composition. In such a case, the log k' *versus* log P plot should fall close to a straight line (equivalent line) representing

$$\log k' = \log P + \log \varphi \tag{4}$$

Fig. 9 shows the plots of log k' *versus* log P for chromium–β-diketonato complexes. The straight line shows the equivalent line (eqn. 4) obtained by the approximate calculation of φ as 0.2 from the carbon content (21%) and the bulk density (0.38 g/cm^3) of the ODS phase used, the column internal volume (2.50 cm^3), the column void volume (1.57 cm^3) and the molar volume of octadecane (327 cm^3/mol, estimated value). All the points in Fig. 9 deviate upwards from the equivalent line. It is noted that the extent of such an upward deviation tends to increase with a decrease in log P.

The solute distribution is generally a function of the energy change accompanying the transfer of a solute from one phase to another. The partition coefficient, P, in this study is given by

$$\log P = -(G_{S,np} - G_{S,p})/2.30RT \tag{5}$$

where G_S is the solution energy for a metal complex, the subscripts p an np indicate the polar liquid phase (methanol–water) and non–polar liquid phase (dodecane), respectively, R is the molar gas constant and T is the temperature. The value 2.30 is the approximate coefficient to give a $\log_{10}$ base equation instead of $\log_e$ base equation.

When the partition concept is applied to the reversed-phase chromatography studied here, the distribution coefficient, K, is discussed in an analogous manner to P and then the following equation is derived from eqn. 3:

$$\log k' = -(G_{S,s} - G_{S,m})/2.30RT + \log \varphi \tag{6}$$

where the subscripts m and s indicate the mobile phase (methanol–water) and the stationary phase (ODS), respectively. As an identical composition of methanol–water is used in the experiments of both partition and chromatography, $G_{S,p} = G_{S,m}$. The fact that all points in Fig. 9 deviate upwards from the equivalent line implies that $G_{S,s} < G_{S,np}$, which means that the transfer of the respective metal complexes from a given methanol–water phase occurs more easily to the ODS phase than to dodecane.

Comparison of the separation factor for the mer–fac pair in chromatography and the liquid–liquid partition

It has been shown in Figs. 5, 6 and 8 that both $\Delta\log k'$ and $\Delta\log P$ are positive for the complexes of fluorinated β-diketones such as tfa, pfa and bzfa, regardless of the composition of the methanol–water phase, whereas they are slightly negative for the complexes of most non-fluorinated β-diketones.

To gain an insight into the influence of the structure of the β-diketonato ligand on the $\Delta\log k'$ observed in the chromatographic separation, the $\Delta\log P$ in the liquid–liquid partition system is discussed in detail.

The solution process can be divided into the following two steps: (1) the formation of a cavity in the solvent to accommodate the solute molecule; and (2) the transfer of the solute molecule into the cavity. These two steps are accompanied by the cavity formation energy (G_C) and the solute-solvent interaction energy (G_i), respectively, which are related to the solution energy, G_s, as follows [19]:

$$G_S = G_C + G_i \qquad (7)$$

The cavity formation energy, G_C, is a function of the size (diameter) of the solute and solvent molecules [19].

This concept has been successfully applied to a discussion of the liquid–liquid partition equilibria of various non-electrolytes [20–22].

When this concept is applied to the liquid–liquid partition of a metal complex, eqn. 5 is rewritten as

$$\begin{aligned}\log P &= -[(G_{C,np} - G_{C,p}) + (G_{i,np} - G_{i,p})]/2.30RT \\ &= -[\Delta G_C + \Delta G_i]/2.30RT \qquad (8)\end{aligned}$$

where ΔG indicates the free energy of transferring a metal complex from the methanol–water phase into dodecane. When the *mer* and *fac* isomers of a complex are regarded as equivalent with respect to their molecular sizes (this means $\Delta G_{C,mer} = \Delta G_{C,fac}$), eqn. 2 is rewritten as

$$\Delta\log P = -[\Delta G_{i,mer} - \Delta G_{i,fac}]/2.30RT \qquad (9)$$

This relationship implies that the separation factor for the *mer–fac* isomer pair depends on the difference in the interaction of the respective isomers with solvents.

In a molecule of the *fac* form of a tris complex with a fluorinated β-diketone, three trifluoromethyl groups with a higher electron withdrawing tendency than the methyl group (Hammet constant $\sigma_P = 0.54$ for $-CF_3$, -0.17 for $-CH_3$) are located at the three edges of one area of the octahedron, which makes this form more polar than

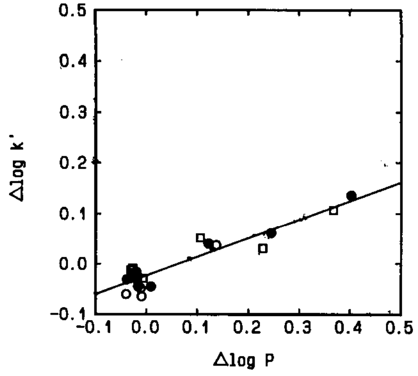


Fig. 10. Correlation between $\Delta\log k'$ and $\Delta\log P$ for geometrical isomers of tris(β-diketonato)–chromium(III). X_{CH_3OH}: ○ = 0.6; ● = 0.8; □ = 1.0.

the *mer* form in which the fluorinated groups are distributed on different sides of the octahedron. For example, the dipole moments of the *fac* and *mer* forms of $Co(tfa)_3$ were reported to be 6.48 and 3.80 D, respectively [23]. It is considered that such a polar *fac* form, compared with the *mer* form, tends to interact strongly with the methanol and/or water which constitutes the polar liquid phase in the partition system, and this causes $\Delta\log P$ to be positive.

In the case of the isomers of a complex with a non-fluorinated β-diketone, the difference in the dipole moment between the *mer* and *fac* forms of the complex is regarded as small, because the electron withdrawing abilities of the functional groups, such as alkyl and phenyl ($\sigma_P = -0.15$ for ethyl, -0.01 for phenyl), are not so considerable as for $-CF_3$, but instead near to that of methyl. Accordingly, the negative extent of the $\Delta\log P$ observed for the complex of such a non-fluorinated β-diketone is attributed not to the dipole–dipole interaction between the complex and the polar liquid phase constituent(s) but to some other kinds of interactions. No particular interaction can be specified at this stage.

Fig. 10 shows that the $\Delta\log k'$ in the chromatography using ODS as the stationary phase is well correlated with $\Delta\log P$ in the liquid–liquid system using dodecane as the non-polar phase ($r = 0.934$; $n = 21$). The linear regression line is given by

$$\Delta\log k' = (0.37 \pm 0.07)\,\Delta\log P - (0.02 \pm 0.01) \qquad (10)$$

This correlation suggests that the chromatographic retention selectivities for the *mer* and *fac* forms are governed by analogous interactions to those affecting the selectivity in the liquid–liquid partition.

It was previously found [7] in work on the retention behaviour of the β-diketonato complexes of chromium(III) and palladium(II) that the capacity factor, k', of a metal complex in the ODS–(methanol–water) system was empirically related to the partition coefficient, P (K_D in paper by Saitoh *et al.* [7]), in the dodecane–(methanol–water) system, as given by the following equations, provides that the same composition of methanol–water is used in both systems

$$\log k' = \log P - p\Delta G_i/2.3RT + q \qquad (11)$$

$$\log k' = (1 + p)\log P + p\Delta G_C/2.3RT + q \qquad (12)$$

where p and q are constants for a given composition of methanol–water.

When these equations are applied to geometrical isomers of the metal complexes studied here, eqn. (12) is modified for the *mer* and *fac* forms, as follows:

$$\log k'_{mer} = (1 + p) \log P_{mer} + p\Delta G_{C,mer}/2.3RT + q \tag{13}$$

$$\log k'_{fac} = (1 + p) \log P_{fac} + p\Delta G_{C,fac}/2.3RT + q \tag{14}$$

When $\Delta G_{C,mer}$ is equal to $\Delta G_{C,fac}$, the following proportional relationship is predicted:

$$\Delta \log k' = (1 + p)\Delta \log P \tag{15}$$

According to the reported values of p (-0.488 to -0.574 at X_{CH_3OH} 0.60–1.00) [7], the proportional coefficient, $(1 + p)$, is predicted in the range 0.426–0.512. It is shown by the experimental plot in Fig. 10 that $\Delta \log k'$ is nearly proportional to $\Delta \log P$. The observed proportional coefficient (strictly, the slope of the regression line), 0.37 ± 0.07, is close to the predicted value. This supports the validity of the empirical equations 11 and 12. It is noted that the slope of the plot of $\Delta \log k'$ *versus* $\Delta \log P$ is smaller than unity (see Fig. 10).

In conclusion with respect to the separation factor for the geometrical isomer pair of tris(β-diketonato)-chromium(III), chromatography in the ODS-(methanol–water) system is inferior to partition in the dodecane-(methanol–water) system, although some exceptions are found.

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