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CHROMATOGRAPHIC SEPARATIONS OF *fac*- AND *mer*-TRIS(β -DIKETONATO)CHROMIUM(III) COMPLEXES

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SUMMARY

In order to find the factors that affect the separation of metal chelates, the elution and distribution behaviour of chromium(III) complexes coordinated with unsymmetrical β -diketones were studied in various solvents using silica gel as an adsorbent. The differences in the specific retention volumes or adsorption distribution coefficients of metal chelates are ascribed to the differences in the total energies of interaction between the chelate molecule and the adsorbent surface. The total energy S^0 is expressed by three independent terms as follows:

$$S^0 = aG_i + bG_j + c$$

where G_i and G_j are parameters representing the interaction energies of the functional groups containing the substituents in a β -diketone. Using the relative values of G_i and G_j for the functional groups, the ratio of the distribution coefficients of $\text{Cr}(\text{acac})_3$ to a tris(β -diketonato)chromium(III) was evaluated. On the basis of a linear relationship between the experimental and calculated distribution coefficients, the quantitative separation of metal chelates in the silica gel adsorption chromatography is discussed.

INTRODUCTION

The chromatographic behaviour of metal chelates has been widely investigated to find the factors that affect the separation of various metal ions¹⁻⁷. In general, the distribution coefficient K_{av} depends on the molar volume of a metal β -diketonate. Also, the separation of geometrical isomers and metal chelates possessing mixed ligands is highly desirable in the field of hot atom chemistry in order to elucidate the reaction mechanisms of recoil atoms in the solid state⁸. However, studies of the separation of the geometrical isomers of metal chelates have so far been limited⁹⁻¹¹.

A trivalent metal ion coordinated with three unsymmetrical bidentate ligands possesses two geometrical isomers that are called *fac*- and *mer*-complexes, as illustrated in Fig. 1. In the *fac*-isomer three R_1 and three R_2 groups are equivalent with respect to a C_3 -axis, whereas the *mer*-isomer has no symmetry. In adsorption chro-

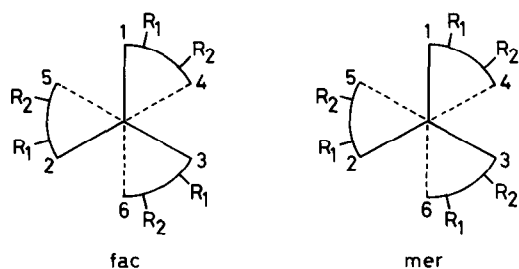


Fig. 1. Configurations of *fac*- and *mer*-isomers of tris(β -diketonato)chromium(III).

matography on a gel, therefore, the *mer*-isomers are eluted in the early fractions and the *fac*-isomers in the later fractions, as expected on the basis of their dipole moments¹².

In this work, the elution and distribution behaviour of various [⁵¹Cr]tris(β -diketonato)chromium(III) compounds was systematically investigated using silica gel as an adsorbent. Seven chelates possessing unsymmetrical ligands and two chelates possessing symmetrical ligands were employed (Table I). The distribution behaviour of mixed ligand complexes possessing acetylacetonone and dibenzoylmethane as symmetrical ligands were also examined.

TABLE I

TRIS(β -DIKETONATO)CHROMIUM(III) CHELATES STUDIED

General formula of the β -diketonates: $R_1COCH_2COR_2$.

No.	Chelate	Abbreviation	R_1	R_2
1	Tris(acetylacetonato)chromium(III)	Cr(acac) ₃	CH ₃	CH ₃
2	Tris(2-furoylacetonato)chromium(III)	Cr(fa) ₃	CH ₃	
3	Tris(2-thenoylacetonato)chromium(III)	Cr(ta) ₃	CH ₃	
4	Tris(benzoylacetonato)chromium(III)	Cr(bzac) ₃	CH ₃	
5	Tris(benzoylfuroylmethanato)chromium(III)	Cr(bfm) ₃		
6	Tris(dibenzoylmethanato)chromium(III)	Cr(dbm) ₃		
7	Tris(2-furoyltrifluoroacetonato)chromium(III)	Cr(fta) ₃		CF ₃
8	Tris(2-thenoyltrifluoroacetonato)chromium(III)	Cr(tta) ₃		CF ₃
9	Tris(benzoyltrifluoroacetonato)chromium(III)	Cr(bta) ₃		CF ₃

EXPERIMENTAL

Reagents

β -Diketones (Dojin Labs., Japan) and the other reagents used were of guaranteed-reagent grade, except for furoylacetone and benzoylfuroylmethane, which were synthesized by modifying the procedures described in the literature^{1,3}.

Synthesis of [⁵¹Cr]tris(β -diketonato)chromium(III)

To a dilute hydrochloric acid solution of potassium dichromate an aqueous [⁵¹Cr]chromate solution was added. The dichromate was reduced to Cr(III) with hydrogen peroxide and the solution was evaporated to dryness. The ⁵¹Cr(III) was refluxed with a β -diketone in aqueous solution. The products were further purified by activated alumina column chromatography.

Column chromatography on silica gel

The ⁵¹Cr-labelled complex in benzene was placed on a silica gel column (Wako Gel C-200, 150 × 11 mm I.D.) and then a suitable eluting agent was supplied at a flow-rate of 0.2 cm³/min. The column was thermostated at 25.0 ± 0.5°C. The eluates, collected in test-tubes, were submitted to radioactivity measurement.

Distribution coefficient measurement

In a specially designed test-tube equipped with a glass stopper, 1 g of silica gel and the desired solvent were placed, then the solution containing the ⁵¹Cr-labelled complex was added. The total volume of the liquid layer was adjusted to 6 cm³ with the solvent. The initial concentration of the complex was less than 2 · 10⁻⁴ M. The mixture was shaken mechanically for 30 min at 20 ± 2°C. A separate experiment showed that equilibrium was attained within 30 min. After centrifuging, an aliquot of the solution was taken and the adsorption distribution coefficient was determined by measuring the radioactivities of the solution and the standard solution of ⁵¹Cr.

Radioactivity measurement

Radioactivity was measured either with a Ge(Li) detector connected to a multi-channel pulse height analyser or with a well-type NaI(Tl) detector connected to a single-channel γ -ray spectrometer.

RESULTS AND DISCUSSION

Optimal conditions for the separation of geometrical isomers were determined using unsymmetrical complexes of Cr(bzac)₃, Cr(ta)₃ and Cr(fta)₃. A typical example of the elution curves of *fac*- and *mer*-Cr(bzac)₃ is shown in Fig. 2. A preliminary study showed that the water content of the silica gel affects the separation factor considerably. Consequently, silica gel with the water content adjusted to 4% was used. The results are summarized in Table II. Skewness from the Gaussian peak shape depends greatly on the composition of the eluent. Thus, complete separation of two geometrical isomers was achieved with 3% (v/v) diethyl ether in benzene for Cr(bzac)₃ and Cr(ta)₃ and with 50% (v/v) benzene in carbon tetrachloride for Cr(fta)₃. However, no satisfactory separations for Cr(fa)₃, Cr(bfm)₃, Cr(tta)₃ and Cr(bta)₃ were achieved.

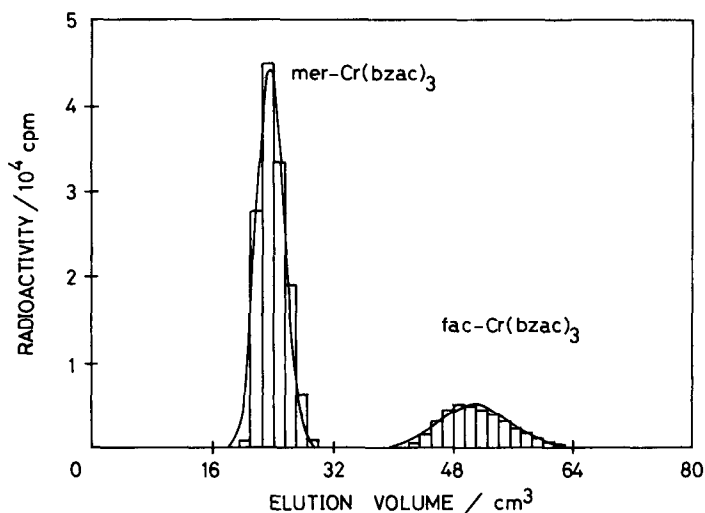


Fig. 2. Elution of tris(benzoylacetonato)chromium(III). Silica gel column (15×1.1 cm I.D.). Eluent: benzene-diethyl ether (97:3). Flow-rate: $0.22 \text{ cm}^3/\text{min}$ at 25°C . Solid lines were calculated by eqn. 8.

The adsorption behaviour of the compounds can be explained fairly well by the equation proposed by Snyder¹⁴:

$$\log R^0 (= \log K_\theta) = \log V_a + \alpha(S^0 - A_s \varepsilon^0) \quad (1)$$

where R^0 is the specific retention volume (cm^3/g), which is defined as the corrected retention volume divided by the weight of adsorbent, K_θ is the sample adsorption distribution coefficient (cm^3/g), which is defined by the ratio of the concentration of

TABLE II

SPECIFIC RETENTION VOLUMES (R^0) OF TRIS(β -DIKETONATO)CHROMIUM(III) CHELATES AT 25°C

Solvent	$R^0 (\text{cm}^3/\text{g})$												
	$Cr(fa)_3$		$Cr(ta)_3$		$Cr(bzac)_3$		$Cr(bfm)_3$	$Cr(fia)_3$		$Cr(tta)_3$		$Cr(bta)_3$	
	mer	fac	mer	fac	mer	fac		mer	fac	mer	fac	mer	fac
$\text{C}_6\text{H}_6\text{-CCl}_4$													
10:90													4.72 sh
20:80											7.58 sh		
50:50								4.42	8.82		1.69 sh		0.49 sh
C_6H_6	181.6	39.3	n.d.**	37.2	n.d.	5.74	sh*	1.11	sh		0.62		0.37
$\text{C}_6\text{H}_6\text{-Et}_2\text{O}$													
97:3	4.51	2.35	7.28	1.86	5.78	0.58		0.58	sh		0.34		0.11
95:5	2.55	1.63	3.94	0.94	2.78	0.23							
93:7	1.63	0.74	1.97	0.74	1.97	0.23							

* sh, shoulder.

** n.d., not determined.

the complex per unit weight of the silica gel to the concentration in unit volume of the solution, V_a is the volume of the adsorbent monolayer (cm^3/g), α is the adsorbent surface activity function, S^0 is the dimensionless free energy of adsorption of a compound on an adsorbent of standard activity ($\alpha = 1.00$), A_s is the molecular area of the adsorbed sample and ϵ^0 is the solvent strength parameter, numerical values of which can be obtained from the table compiled by Snyder¹⁴.

In order to apply eqn. 1 to the present system, the column parameters (V_a and α) must be determined first. If solutes of known S^0 values are eluted with *n*-pentane ($\epsilon^0 = 0$), a plot of $\log R^0$ against S^0 should give a straight line of slope α and intercept $\log V_a$. As Fig. 3 shows, a straight line was obtained when benzene, toluene, naphthalene, phenanthrene and dibenzyl were used as solutes. Thus, α and V_a were determined to be 0.644 and $0.149 \text{ cm}^3/\text{g}$, respectively, for the column used.

For the evaluation of other parameters such as S^0 and A_s , it is very difficult to determine R^0 over the wide range of ϵ^0 . In an ideal system, however, R^0 should be replaced by K_g , as is shown in eqn. 1. Two experiments were performed in order to obtain the relationship between R^0 and K_g . As Fig. 4 shows, a linear plot of the concentration of *fac*-Cr(ta)₃ in the adsorbent against that in the solution, together with a similar relationship for *mer*-Cr(ta)₃, provides evidence in confirmation of adsorption equilibrium at least below $10^{-4} M$. Further, the fact that the straight line passes through the origin excludes the possibility of chemisorption of the chelates on the adsorbent. The correlation between $\log R^0$ and $\log K_g$ was determined using Cr(fa)₃, *mer*-Cr(ta)₃, *mer*-Cr(bzac)₃ and Cr(bfm)₃ in benzene and benzene-diethyl ether systems. On the basis of the experimental observation of a linear relationship between $\log R^0$ and $\log K_g$, as shown in Fig. 5, K_g can generally be used instead of R^0 .

The adsorption distribution coefficients of various chelates were determined by varying the solvent strength parameters from $\epsilon^0 = 0.11$ (CCl_4) to 0.32 (CH_2Cl_2). The results are summarized in Figs. 6 and 7. When diethyl ether is present in the

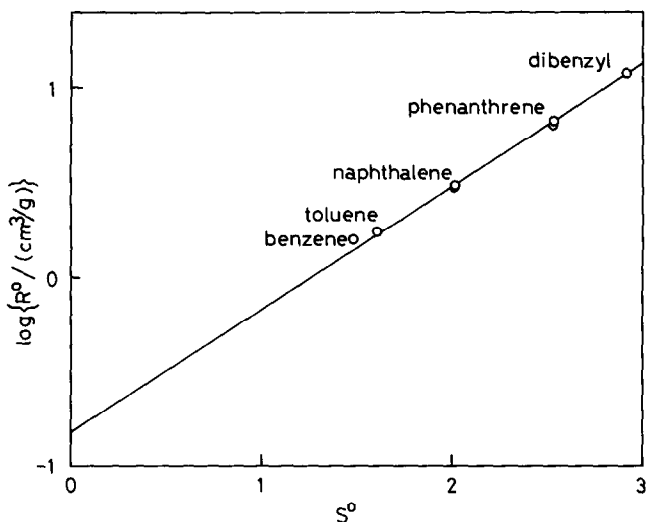


Fig. 3. Determination of α and V_a .

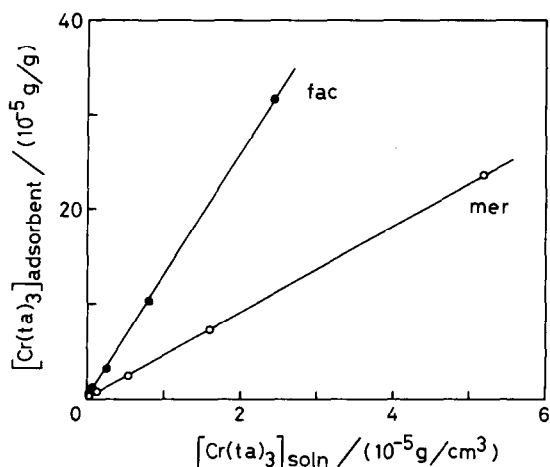


Fig. 4. Equilibrium adsorption of *fac*- and *mer*-Cr(ta)₃ distributed between the silica gel and benzene-diethyl ether (97:3).

binary mixtures, the dependence of $\log K_g$ on ε^0 apparently differs from that in the other systems. Consequently, the discussion will be concentrated mainly on the system carbon tetrachloride-benzene-dichloromethane. As can be seen in Fig. 7, the plots of $\log K_g$ against ε^0 are linear with the same slope for all the chelates studied, although the slope for a given chelate in the carbon tetrachloride-benzene system tends to be slightly different from that in the benzene-dichloromethane system. Ac-

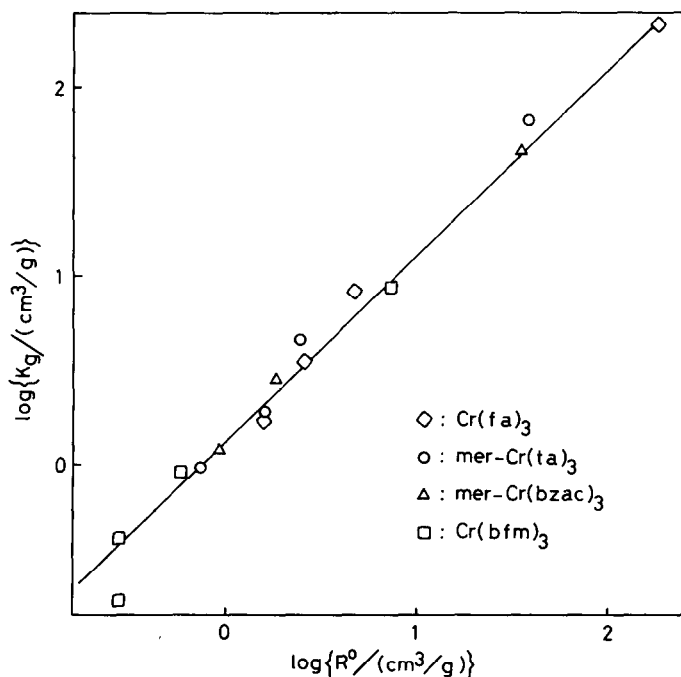


Fig. 5. Relationship between $\log K_g$ and $\log R^0$ in benzene and benzene-diethyl ether systems.

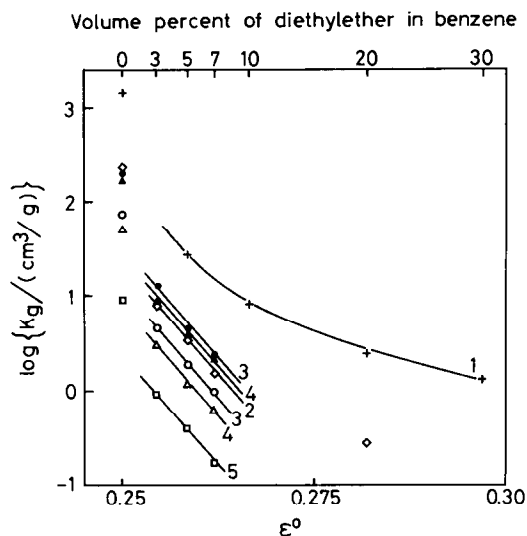


Fig. 6. Dependence of $\log K_g$ on ϵ^0 in the benzene-diethyl ether system. Numerals correspond to chelates in Table I. Closed symbols: *fac*-isomer. Open symbols: *mer*-isomer.

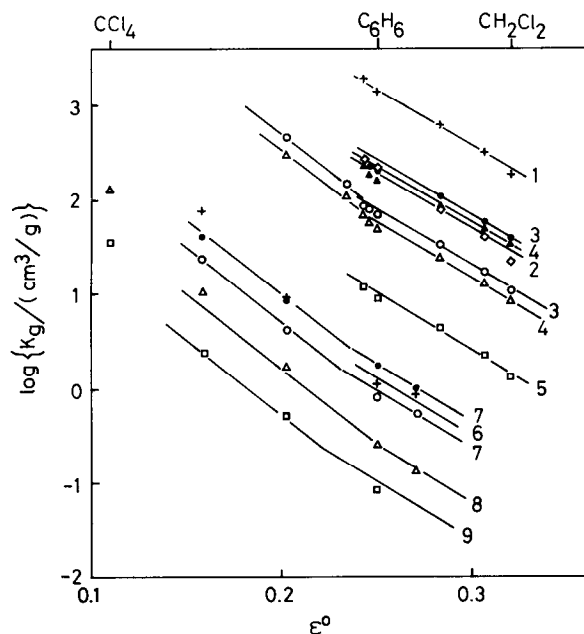


Fig. 7. Dependence of $\log K_g$ on ϵ^0 in the carbon tetrachloride-benzene-dichloromethane system. Numerals correspond to chelates in Table I. Closed symbols: *fac*-isomer. Open symbols: *mer*-isomer.

According to eqn. 1, the same slope means that the molecular area of the adsorbed chelates, A_s , is constant for all the chelates, irrespective of the different molecular volumes⁵.

The total energy of interaction between the molecule of a compound and the adsorbent surface is given by the sum of the energies of interaction of a constituent group i in the molecule with the surface as follows:

$$S^0 = \sum_i Q_i^0 \quad (2)$$

where Q_i is defined as the dimensionless free energy of adsorption of a group i (ref. 14). In the chelate molecule, however, the situation will become more complicated and the accumulated Q_i^0 values cannot be applied directly to the present system, because a number of possible sites for adsorption may exist.

As can be clearly seen in Fig. 7, when one of the substituents (R_1) in the ligand is a methyl group and the other (R_2) is varied, the $\log K_g$ value decreases at constant ϵ^0 in the order $R_2 = \text{methyl} > \text{furyl} > \text{thienyl} > \text{phenyl}$. A similar trend can also be found when R_1 is replaced by CF_3 . The difference in K_g for various tris(β -diketonato)chromium(III) complexes is larger than that for different metal complexes with specified ligands¹⁰. These features support the idea that the distribution of the chelate is predominantly governed by the interaction of coordinated ligands with the adsorbent and the central metal ion would be highly screened.

Taking into account the maximal distribution coefficient in $\text{Cr}(\text{acac})_3$ and the weak interaction of the methyl group with silica gel¹⁴, the interaction site in the complex is reasonably assumed to be the carbonyl group on which the electron density is affected by the substituent. This is further supported in terms of the constant A_s in tris(β -diketonato)chromium(III).

Thus, S^0 is assumed to be composed of three independent terms as follows:

$$S^0 = aG_i + bG_j + c \quad (3)$$

where G_i and G_j are parameters representing the interaction energies of the functional groups containing the substituents R_i and R_j , respectively, and a , b and c are constants. The constant c results from the minor contribution of the central metal ion, but it can be eliminated by taking the difference in $\log K_g$ for two chelates. Further assumptions may be made that three ligands contribute at the same time to adsorption, in which the preferential orientation of the stronger functional group would result so long as the geometrical arrangement permits it, *i.e.*, the functional groups in positions 1, 3 and 5 as designated in Fig. 1.

In fact, no satisfactory results were obtained by statistical treatments assuming that three adjacent substituent groups, for example, 1, 2 and 3 as designated in Fig. 1, interact randomly with the adsorbent surface on the silica gel. In addition, the idea that only one or two ligands participate in adsorption cannot explain the different behaviour in the distribution of *fac*- and *mer*-complexes.

If the interactions are governed only by three functional groups containing a methyl group, differences in the distribution coefficients cannot be reasonably explained for the *fac*-complexes of $\text{Cr}(\text{fa})_3$, $\text{Cr}(\text{ta})_3$ and $\text{Cr}(\text{bzac})_3$. Consequently, the functional groups that are situated in the bulk of solvent should play a role in the

adsorption of complex. On the basis of these considerations, one assumes simply that a functional group contributes to one third of the attractive interaction, and it acts in a reverse manner when it is situated at the opposite site. The positive interaction term for the group i is expressed as $G_i/3$, and the negative term one is tentatively defined as $-b(k - G_i)/3$, where k is a constant. Thus, for Cr(acac)₃:

$$S^0/\alpha = G_{\text{CH}_3} - b(k - G_{\text{CH}_3}) + c \quad (4)$$

and for fac-Cr(bzac)₃:

$$S^0/\alpha = G_{\text{CH}_3} - b(k - G_{\text{C}_6\text{H}_5}) + c \quad (5)$$

where the subscripts CH₃ and C₆H₅ indicate the functional groups containing methyl and phenyl groups, respectively. From eqn. 1, the following equation is derived for constant ε^0 and A_j :

$$\Delta \log K_g = \log K_{g,1} - \log K_{g,2} = \alpha(S_1^0 - S_2^0) = \alpha \Delta S^0 \quad (6)$$

where the subscripts 1 and 2 refer to chelates 1 and 2, respectively. When Cr(acac)₃ is chosen as a reference chelate, $\Delta \log K_g$ can be expressed in various systems as summarized in Table III. In a given chelate, $\Delta \log K_{g,mf} = \log K_{g,fac} - \log K_{g,mer}$ is given by

TABLE III

DIFFERENCE IN THE LOGARITHMIC DISTRIBUTION COEFFICIENTS BETWEEN Cr(acac)₃ AND Cr(β -dik)₃

$$\Delta \log K_g = \log K_{g,\text{Cr}(\text{acac})_3} - \log K_{g,\text{Cr}(\beta\text{-dik})_3}$$

Complexes	$\Delta \log K_g/\alpha^*$	
Single ligand complexes	(a) $R_i \neq R_j$: fac: $(1 + b)G_{\text{CH}_3} - G_i - bG_j$ mer: $(1 + b)G_{\text{CH}_3} - \frac{1}{3}(2 + b)G_i - \frac{1}{3}(1 + 2b)G_j$	
	(b) $R_i (= \text{CH}_3) \neq R_j$: fac: $b(G_{\text{CH}_3} - G_j)$ mer: $\frac{1}{3}(1 + 2b)(G_{\text{CH}_3} - G_j)$	
	(c) $R_i = R_j (\neq \text{CH}_3)$: $(1 + b)(G_{\text{CH}_3} - G_j)$	
	Mixed ligand complexes [Cr(acac) _{3-n} (dbm) _n]	(a) Cr(acac) ₂ (dbm): $\frac{1}{3}(1 + b)(G_{\text{CH}_3} - G_{\text{C}_6\text{H}_5})$
		(b) Cr(acac)(dbm) ₂ : $\frac{1}{3}(1 + b)(G_{\text{CH}_3} - G_{\text{C}_6\text{H}_5})$
		(c) Cr(dbm) ₃ : $(1 + b)(G_{\text{CH}_3} - G_{\text{C}_6\text{H}_5})$

* α = Adsorbent surface activity function.

$$\Delta \log K_{g,mf} = \alpha \left(\frac{1-b}{3} \right) (G_i - G_j) \quad (7)$$

The following relation holds experimentally:











$$\Delta \log K_{g,mf} > 0$$

and if G_i is larger than G_j , the constant b must satisfy the criterion $0 < b < 1$.

Similar relationships for the mixed ligand complexes can be derived. In Table III, examples of $\text{Cr}(\text{acac})_{3-n}(\text{dbm})_n$ are also listed where both ligands are symmetrical.

When G_{CH_3} is chosen as a reference and let $G_{\text{CH}_3} = 5$, the values of G_j are determined by using experimental values of $\Delta \log K_g$. The value of b for obtaining

TABLE IV
CALCULATED $\Delta \log K_g$ VALUES FOR VARIOUS TRIS(β -DIKETONATO)CHROMIUM(III) CHELATES

R_i	R_j	G_i	G_j	$\Delta \log K_g$			
				<i>fac</i>		<i>mer</i>	
				<i>Exptl.</i>	<i>Calcd.</i>	<i>Exptl.</i>	<i>Calcd.</i>
CH ₃	CH ₃	5.00	5.00	—	—	—	—
CH ₃		5.00	3.74	—	0.57	0.80	0.80*
CH ₃		5.00	3.09	0.84	0.86	1.21	1.21*
CH ₃		5.00	2.93	0.93	0.93	1.40	1.31
		3.74	2.93	—	2.19	2.21	2.34
		2.93	2.93	3.00	3.00*	—	—
	CF ₃	3.74	1.57	2.87	2.81	3.16	3.20
	CF ₃	3.09	1.57	—	3.45	3.73	3.73*
	CF ₃	2.93	1.57	—	3.61	4.01	3.86
Mixed ligand complexes:							
Cr(acac) ₂ (dbm)				0.97	1.00		
Cr(acac)(dbm) ₂				2.00	2.00		

* The experimental value of the complex was used for the determination of G_j .

the best fit between the observed and calculated distribution coefficients was determined to be 0.45. The results are summarized in Table IV.

Eqn. 3 was introduced under the condition that the electronic structure of the functional group i must remain independent of the structure of the remainder of the chelate ring¹⁴. The validity of this prerequisite is clearly shown by the linear relationship between the calculated and experimental values of $\Delta \log K_g$, as is shown in Fig. 8. This linear relationship holds even in the diethyl ether-benzene (5:95) system. Consequently, the different dependence of $\log K_g$ on ϵ^0 in the diethyl ether-containing system (Fig. 6) may be ascribed to the difference in the $A_s \epsilon^0$ term.

It must be noted, of course, that the values of G_j obtained are in arbitrary units and have to be multiplied by a factor in order to obtain the real free energy. In addition, additivity of the adsorption free energy of each sample group as expressed by eqn. 2 fails in the present chelate complex system. In organic molecules, A_s is also given by the sum of the areas of each sample group¹⁴. In chelate molecules, however, the dominant factors governing the adsorption seem to be the electronic density on a carbonyl group in the chelate ring and the area of the interaction sites. Consequently, the apparent role of a substituent in the ligand is to bring about an electronically induced change in the adsorption energy at the interaction sites. It is noteworthy that according to eqn. 7, the separation of *fac*- and *mer*-isomers is governed principally by the difference between G_i and G_j , irrespective of the magnitude of K_g .

If the ratio $K_{g, \text{fac}}/K_{g, \text{mer}}$ is high, separation of two complexes can easily be achieved. However, there still remains the question of whether a satisfactory separation of two complexes can be achieved under a given set of conditions. From the viewpoint of plate theory, a comparatively simple equation for elution can be derived as follows¹⁵:

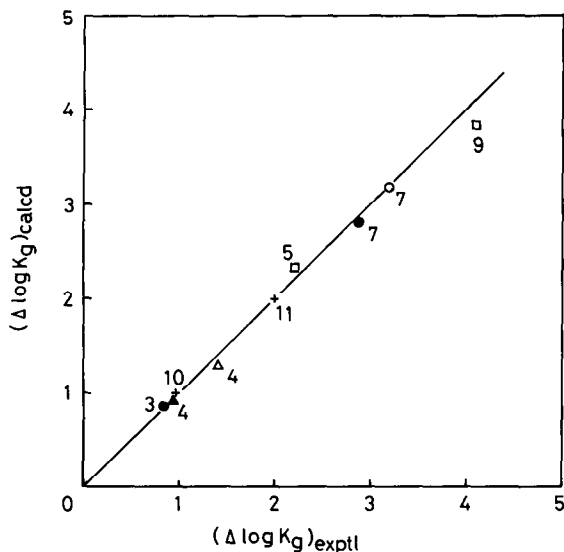


Fig. 8. Comparison of experimental and calculated values of $\Delta \log K_g$. Nos. 3-9 correspond to chelates in Table I; 10 = $\text{Cr}(\text{acac})_2(\text{dbm})$; 11 = $\text{Cr}(\text{acac})(\text{dbm})_2$.

$$\begin{aligned}
 M &= M^* \exp \left[-\frac{p(1+C)}{2} \left(\frac{U-U^*}{U^*} \right)^2 \right] \\
 &= M^* \exp \left[-2.773 \left(\frac{U-U^*}{W} \right)^2 \right]
 \end{aligned} \tag{8}$$

where M is the concentration of a solute in the eluent at the elution volume U , p is the number of plates in the column, W is the peak width at half-maximum and C is the distribution ratio, *i.e.*, the amount of a solute in the stationary phase of any plate divided by the amount of the same solute in the mobile phase of the same plate at equilibrium. Thus, C is related to K_d by the equation

$$C = K_d w/v \tag{9}$$

where w and v are the weight of the silica gel and the volume of liquid phase in any plate. The asterisks in eqn. 8 refer to the peak. The retention volume is also given by

$$U^* = V(1 + C) \tag{10}$$

where V is the interstitial volume of the column.

As illustrated in Fig. 2, the calculated elution curves appear to be comparable to the observed curves, in spite of slight asymmetry. Therefore, calculations based on plate theory are allowed, giving an equation for the quantitative separation of two complexes. Assuming that separation is quantitative if there is not more than 0.1% cross-contamination, the elution volume U_i at which two elution curves intersect is derived as follows:

$$U_i = U^* + 1.32W$$

Taking into consideration that

$$W = 2.355U^* \sqrt{\frac{C}{p(1+C)}}$$

and C_2 is assumed to be larger than C_1 , the following condition should be required for quantitative separation:

$$(1 + C_1) \left[1 + 3.09 \sqrt{\frac{C_1}{p(1 + C_1)}} \right] \leq (1 + C_2) \left[1 - 3.09 \sqrt{\frac{C_2}{p(1 + C_2)}} \right] \tag{11}$$

For various values of p , minimum ratios of C_2 to C_1 that satisfy eqn. 11 were calculated for various C_1 values and the results are given in Fig. 9. It is obvious that the ease of separation of two complexes depends on the ratio C_2/C_1 . Although the absolute values of the distribution ratios are also important, the feature that the ratio

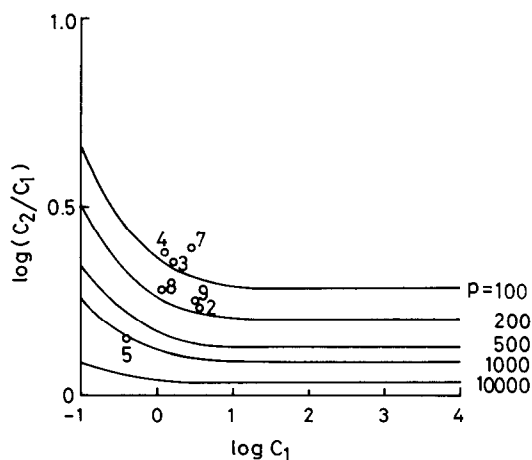


Fig. 9. Minimum value of $\log(C_2/C_1)$ for quantitative separation of two compounds at constant p and separation of *fac*- and *mer*-tris(β -diketonato)chromium(III) complexes. Numerals correspond to chelates in Table I. Eluents: 2-5, benzene-diethyl ether (97:3); 7 and 8, benzene-carbon tetrachloride (50:50); 9, benzene-carbon tetrachloride (10:90).

C_2/C_1 becomes constant at higher C_1 values suggests that an improvement in the separation factor may be effected by using a long column, except for any pair of complexes with $\Delta \log C$ less than 0.026. The number of plates in the column was determined to be 97.0. Consequently, the finding that, as illustrated in Table II, satisfactory separations of *fac*- and *mer*-complexes for $\text{Cr}(\text{ta})_3$ and $\text{Cr}(\text{bzac})_3$ are possible, whereas separation is incomplete for $\text{Cr}(\text{fa})_3$, can be understood by inspection of Fig. 9.

The present interaction model can predict the most favourable conditions for the separation of various tris(β -diketonato)chromium(III) complexes. However, it would be effective only in the silica gel system, because different orders of elution of metal chelates were found in gel adsorption chromatography². Although the order of G values is coincident with that of Hammett σ values¹⁶, further studies on the determination of these absolute values, with implications for the physico-chemical nature and effect of the central metal ion, are desirable.

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