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CLAY COLUMN CHROMATOGRAPHY FOR OPTICAL RESOLUTION OF TRIS(CHELATED) AND BIS(CHELATED) COMPLEXES ON A Λ-Ru(1,10-PHENANTHROLINE)$_3^{2+}$-MONTMORILLONITE COLUMN

AKIHIKO YAMAGISHI

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060 (Japan)

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SUMMARY

The chromatographic resolution of tris(chelated) and bis(chelated) complexes was investigated on a Λ-Ru-tris(1,10-phenanthroline)$^{2+}$ (Λ-Ru(phen)$_3^{2+}$)–montmorillonite column. The following complexes were resolved partially when they were eluted with the solvents denoted in square brackets: [water] Co(acac)$_3$ (acac = acetylacetonate), Co(acac)$_2$(glycinate), Co(acac)$_2$(D,L-alaninate), Cr(acac)$_2$(glycinate), Co(dimethylglyoximate)$_3$, Co(phen)(glycinate)$_2^+$, Co(acac)$_2$(ethylenediamine)$^+$, Co(acac)$_2$(NH$_3$)$_2^+$, Co(1-nitroso-2-naphthol-3,6-disulphonate)$_3^{6-}$, As(catecholate)$_3^-$ and Co(4-(2-pyridylazo)resorcinol)$_2^+$; [water–methanol] Cr(acac)$_3$ and Rh(acac)$_3$; [ethanol] Co(1-(2-pyridylazo)-2-naphthol)$_2^+$, Co(2-(2-pyridylazo)-1-naphthol)$_2$ and Co(2-(5-chloro-2-pyridylazo-5-diethylaminophenolate)$_2^+$; [chloroform] Cr(3-nitroacetylacetonate)$_3$. The results demonstrate the wide applicability of the present type of clay column for the resolution of racemic metal chelates.

INTRODUCTION

Recently I initiated liquid column chromatography using a clay–metal chelate adduct as packing material[1,2]. The development of this method was motivated by the finding that a certain kind of tris(chelated) complex formed a stereoregular adsorbate layer inside the interlayer region of a clay[3]. For example, when tris(1,10-phenanthroline)iron(II), Fe(phen)$_3^{2+}$, was adsorbed on colloidally dispersed sodium montmorillonite, the Λ- and Δ-enantiomers of the chelate were stacked in stereoregular ways[3-5]. Similar behaviour was observed even between enantiomers of different kinds such as Λ-Fe(phen)$_3^{2+}$ and Δ-Ni(phen)$_3^{2+}$. Thus it was concluded that, once a clay is modified by an enantiomer of an optically active metal chelate, the material acts as an adsorbent capable of resolving other racemic mixtures. Clay column chromatography based on the above principle succeeded in resolving tris(acetylacetonato)metal(III) complexes, M(acac)$_3$, on a column of Δ-Ni(phen)$_3^{2+}$-montmorillonite[2]. Most probably, M(acac)$_3$ was adsorbed either by the side of or over the head of preadsorbed Δ-Ni(phen)$_3^{2+}$, depending on whether the chelate had the Λ- or Δ-configuration, respectively[2].

The present paper describes the further application of clay column chromato-

graphy, using a column of Λ-Ru(phen)$_3^{2+}$–montmorillonite. Here Λ-Ru(phen)$_3^{2+}$ was chosen because it is negligibly racemized at room temperature, thus prolonging the resolution ability of a column[6].

EXPERIMENTAL

The solid Λ-Ru(phen)$_3^{2+}$–montmorillonite (<70 mesh) was prepared as described previously[6]. About 67% of the Na$^+$ in sodium montmorillonite was replaced with Λ-Ru(phen)$_3^{2+}$, the residual sites being occupied by Na$^+$. Λ-Co(phen)$_2$ (L-valinate)$^{2+}$–montmorillonite was prepared by mixing sodium montmorillonite and Λ-Co(phen)$_2$(L-valinate)SO$_4$. In this case, all the Na$^+$ was replaced with Λ-Co(phen)$_2$(L-valinate)$^{2+}$. The resultant pink material was dried and ground into a powder (<70 mesh).

The following complexes were prepared according to the literature: tris(3-nitroacetylacetonato)chromium(III)[7]; Co(acac)$_2$(en)ClO$_4$ (en = ethylenediamine)[8]; Co(acac)$_2$(NH$_3$)$_2$I[9]; Co(phen)(glycinate)$_2$Br[10]; tris(dimethylglyoximato)cobalt(III)[11]; Cr(phen)$_2$(ox)Cl (ox = oxalate)[12]; Cr(phen)$_2$Cl$_3$[13]; mer-Co(glycinate)$_3$[14]; mer-Co(D,L-alaninate)$_3$[14]; KAs(catecholate)$_3$·H$_2$O[14]; Zn(8-hydroxyquinoline-5-sulphonate)$_2$[15]; a solution of Λ-Co(phen)$_2$(L-valinate)SO$_4$[16]. Cr(acac)$_2$(glycinate) was prepared by a method similar to that in ref. 17. Tris(8-quinolinolato)aluminium(III) was prepared by mixing the ligand in ethanol with Al^{3+} in water. The solutions of the following complexes were prepared by mixing the equivalent amounts of metal chloride and ligand in either water or ethanol: tris(1-nitroso-2-naphthol-3,6-disulphonato)-cobaltate(III); bis[4-(2-pyridylazo)resorcinol]cobalt(III); bis[1-(2-pyridylazo)-2-naphthol]cobalt(III); and bis[2-(2-pyridylazo)-1-naphthol]cobalt(II). Bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) chloride was purchased from Dojindo Lab. (Japan). The preparation of other complexes was described previously[18].

The chromatographic procedures were carried out at room temperature. Usually, a chelate was loaded on a column in 1 ml of an appropriate solvent; otherwise, the details are described in the text. The optical rotatory dispersion (ORD) and circular dichroism (CD) curves were recorded on a JEOL Model ORD/CD-5 optical rotatory spectrometer. The electronic absorption spectra of an effluent were measured with a EPS-3T spectrophotometer. X-ray diffraction measurements were performed with a Toshiba XC-40H apparatus. High-performance liquid chromatography (HPLC) was carried out with a Hitachi liquid chromatograph, Type 635 equipped with a Waters Model U6K injector. Chromatograms were obtained by recording the absorbance of an effluent at a constant wavelength against time.

RESULTS

The following five groups of metal chelates were placed on a Λ-Ru(phen)$_3^{2+}$–montmorillonite column in order to investigate the resolution ability of the column; (i) M(III)(acac)$_3$, M(III)(acac)$_2$(aa), aa = neutral or negative bidentate ligand, and M(III)(acac)$_2$X$_2$; (ii) M(II)(phen)$_2$(aa), M(II)(phen)$_2$X$_2$ and M(II)(phen)-(aa)$_2$; (iii) M(III)(bb)$_3$, bb = dimethylglyoximate and 8-quinolinolate; (iv) M(III)(cc)$_3$, cc = 8-hydroxyquinoline-5-sulphonate, catecholate and 1-nitroso-2-naphthol-3,6-disulphate; (v) Co(II)(ddd)$_2$ and Co(III)(ddd)$_2$, ddd = terdentate pyridylazo-ligand. The

first and second groups were selected because the acetylacetonato and 1,10-phenan-throline ligands were expected to enhance affinity toward the present type of column[1,4]. The third group was investigated because these neutral chelates were not completely resolved by other known methods. The fourth and fifth groups were chosen in order to extend the resolution ability to negative tris(bidentate) and bis(terdentate) chelates, respectively.

Resolution of tris(acetylacetonate)metal(III)

The complexes $Co(acac)_3$, $Cr(acac)_3$, $Rh(acac)_3$ and $Cr(3\text{-nitroacetylacetonate})_3$ were loaded on a Λ-$Ru(phen)_3^{2+}$–montmorillonite column and eluted with various kinds of solvents, depending on their solubilities. The chromatographic results are sum-marized in Tables I and II. The following points are noteworthy. (1) $Rh(acac)_3$ was resolved at as high as 83% of optical purity. The same chelate was, however, resolved on a Δ-$Ni(phen)_3^{2+}$–montmorillonite column only to a small extent ($<1\%$)[2]. In this respect, $Ru(phen)_3^{2+}$ is superior to $Ni(phen)_3^{2+}$ as a preadsorbate in recognizing the chirality of tris(acetylacetonato) chelates. (2) When $Co(acac)_3$ was eluted with water, the Λ-isomer was eluted first followed by the Δ-isomer. This order was reversed when water–methanol (2:1 v/v) was employed as eluent. The results are difficult to interpret in terms of competitive adsorption on the same binding site (see Discussion). (3) $Cr(a-cac)_3$ was resolved to a measurable extent with both 95% (v/v) methanol and chloro-form. The results give promise that even an organic molecule hardly soluble in water could be resolved on the present column*. (4) When $Cr(acac)_3$ was eluted with chlo-roform, the Δ-$Cr(acac)_3$ appeared first. On the other hand, when $Cr(3\text{-nitroacetyla-cetonate})_3$ was eluted with the same solvent, the Λ-isomer of the complex appeared initially. The results imply that a slight change in the ligand structures has a significant effect on which of the optical isomers of a resolved chelate is preferred by the column.

Resolution of other acetylacetonate complexes

The following bis(acetylacetonato) complexes were loaded on a Λ-Ru-$(phen)_3^{2+}$–montmorillonite column: $Co(acac)_2(glycinate)$; $Co(acac)_2(D,L\text{-alaninate})$; $Cr(acac)_2(glycinate)$; $Co(acac)_2(en)ClO_4$ and $Co(acac)_2(NH_3)_2I$. The first two neutral complexes were resolved on a Δ-$Ni(phen)_3^{2+}$–montmorillonite column, but the last two positively charged chelates were not[2]. The chromatographic results are summarized in Table III. As shown, all of the loaded chelates were resolved partially on the present column, $Cr(acac)_2(glycinate)$ being resolved for the first time. The UV and CD spectra of the initial effluents are shown in Fig. 1. Since the spectra are roughly similar to those of Λ-$Cr(acac)_2(D,L\text{-alaninate})$[17], the effluent contained an excess of the Λ-$Cr(acac)_2(glycinate)$ enantiomer. For all the neutral bis(acetylacetonato) chelates, therefore, the Δ-isomers are bound to the column more firmly than are the Λ-isomers. Similar behaviour was shown by $Co(acac)_2(glycinate)$ and $Co(acac)_2$ (D,L-alaninate) on a Δ-$Ni(phen)_3^{2+}$–montmorillonite column[2].

When $Co(acac)_2(en)ClO_4$ and $Co(acac)_2(NH_3)_2I$ were eluted with water, the sign of the molecular rotation around 540 nm of the effluent was constant, indicating an

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* In fact, 2,3-dihydro-2-methyl-5,6-diphenylpyrazine was resolved on the same column when the compound was eluted with methanol–water(1:2)[19].

TABLE I

CHROMATOGRAPHIC RESULTS FOR M(acac)$_3$ ON A Λ-Ru(phen)$_3{}^{2-}$–MONTMORILLONITE COLUMN

Chelate amount (mole)	Eluent	Volume of fraction (ml)	Concentration (10^{-3}M)	Molecular rotation and wavelength (nm)	Resolution (%) and enantiomer in excess	Column size (cm × cm O.D.)
Co(acac)$_3$	Water	2	0.8	− 19,000 (480)	61 (Λ)	0.5 × 1
(8 · 10^{-6})		2	0.8	− 13,000	43 (Λ)	
		2	0.5	+ 2000	7 (Δ)	
		2	0.2	+ 18,000	60 (Δ)	
		2	0.1	+ 20,000	67 (Δ)	
	Methanol	2	0.7	+ 21,000	70 (Δ)	
Co(acac)$_3$	Water–methanol	2	1.3	+ 2000 (480)	7 (Δ)	1 × 1
(6 · 10^{-5})	(2:1)	2	7.8	+ 300	1 (Δ)	
		2	1.0	0	0	
		2	0.7	− 3000	10 (Λ)	
Cr(acac)$_3$	Water–methanol	2	1.7	− 2800 (570)	20 (Δ)*	0.5 × 1
(1.2 · 10^{-5})	(2:1)	2	2.3	+ 800	6 (Λ)	
		2	0.5	+ 7000	50 (Λ)	
Cr(acac)$_3$	95% Methanol	2	8.0	− 300 (570)	2 (Δ)*	0.5 × 1
(2.2 · 10^{-5})		2	2.3	+ 800	6 (Λ)	
Cr(3-NO$_2$-acac)$_3{}^{\star\star}$	Chloroform	2	4.3	+ 320 (570)	(Λ)	1 × 1
(5.6 · 10^{-5})		2	4.3	+ 50	(Λ)	
		2	8.6	0		
		2	10.0	− 50	(Δ)	
		2	1.4	− 710	(Δ)	
Rh(acac)$_3$	Water–methanol	1	0.8	+ 5900 (433)	50 (Δ)***	2 × 1.2
(8.0 · 10^{-6})	(2:1)	1	11.5	+ 4000	33 (Δ)	
		2	7.3	+ 2600	22 (Δ)	
		2	4.1	− 2900	24 (Λ)	
		6	2.7	− 6300	52 (Λ)	
		4	1.6	− 10,000	83 (Λ)	

* Based on [M]$_{570}$ = − 14,000 [Δ-Cr(acac)$_3$] and + 14,000 [Λ-Cr(acac)$_3$]. These values were obtained by comparing the ORD and CD spectra of the same solution (c.f., ref. 28).

** 3-NO$_2$-acac denotes 3-nitroacetylacetonate.

*** Based on [M]$_{433}$ = +11,800 [Δ-Rh(acac)$_3$] and −11,800 [Λ-Rh(acac)$_3$]. The values were estimated as in footnote *.

excess of the Δ-isomers of these chelates. The enantiomers of opposite configuration are bound to the column so firmly that they were not separated even with 0.1 M sodium chloride, methanol or ethanol. They are likely to occupy the cation-exchange sites of the column, so displacing Na$^+$ into the eluent.

Bis- and mono(1,10-phenanthroline) complexes

The following 1,10-phenanthroline complexes were loaded on a Λ-Ru(phen)$_3{}^{2+}$–montmorillonite column: Co(phen)(glycinate)$_2$Br, Cr(phen)$_2$Cl$_3$ and

TABLE II

RETENTION VOLUMES AND SEPARATION FACTORS FOR THE RESULTS IN TABLE I

Volumes I and II indicate the peak positions in the concentration *versus* elution volume curves for the initially and finally eluted enantiomers, respectively. The separation factor is defined as volume II divided by volume I.

Complex	Eluent	Volume I (ml)	Volume II (ml)	Separation factor, f_s
Co(acac)$_3$	Water	3.3	5.6	1.7
Co(acac)$_3$	Water–methanol (2:1)	2.0	2.2	1.1
Cr(acac)$_3$	Water–methanol (2:1)	3.5	4.5	1.3
Cr(acac)$_3$	95% Methanol	2	< 3	< 1.2
Cr(3-NO$_2$-acac)$_3$	Chloroform	2	< 3	< 1.2
Rh(acac)$_3$	Water–methanol (2:1)	2.0	3.0	1.5

Cr(phen)$_2$(ox)Cl. The results for Co(phen)(glycinate)$_2$Br are given in the last column of Table III. Only Λ-Co(phen)(glycinate)$_2{}^+$ was eluted and its antipode was not recovered with 0.1 M NaCl solution. For Cr(phen)$_2$Cl$_2{}^+$ and Cr(phen)$_2$(ox)$^+$, no chromium complexes were eluted with water. Instead, the effluent contained Λ-Ru(phen)$_3{}^{2+}$, indicating that the loaded chelates were adsorbed by the column, displacing preadsorbed Λ-Ru(phen)$_3{}^{2+}$. Thus these chromium enantiomers were not resolved because the Δ- and Λ-enantiomers showed the same affinity for the cation-exchange sites of the clay.

Resolution of tris(dimethylglyoximato)cobalt(III)

Tris(dimethylglyoximato)cobalt(III), Co(DH)$_3$, first synthesized in 1954 has resisted attempts at its resolution into two optical isomers[11]. The difficulty may lie in the fact that the complex is inert, forming no diastereomer with resolving agents. The preceding successful resolutions indicated the possibility of resolving Co(DH)$_3$, because it has six methyl groups just like Co(acac)$_3$.

$3 \cdot 10^{-5}$ mole of Co(DH)$_3 \cdot$ 2.5 H$_2$O in 2 ml of water were placed on a 2 × 1.2 cm O.D. column of Λ-Ru(phen)$_3{}^{2+}$–montmorillonite. The chelate was eluted with water, resulting in the appearance of optical rotation in the range of 200–600 nm. The chromatographic data are given in Table IV. The upper and lower curves in Fig. 2 show the CD and UV spectra respectively at the elution volume of 20 ml. At this stage, the optical rotation at 470 nm has already changed to a negative value. Thus, the circular dichroism is due to the enantiomer showing the stronger affinity toward the column. The positive and negative peaks at 275 and 250 nm, respectively, may be assigned to the exciton-splitting π–π^* transitions as in Co(acac)$_3{}^{20}$.

The absorption and CD spectra were both affected by the proton concentration of the solvent (curves 1–3 in Fig. 2). This is probably due to the following protonation and deprotonation equilibria
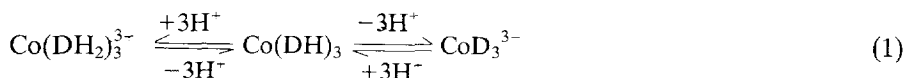
$$Co(DH_2)_3^{3-} \underset{-3H^+}{\overset{+3H^+}{\rightleftharpoons}} Co(DH)_3 \underset{+3H^+}{\overset{-3H^+}{\rightleftharpoons}} CoD_3^{3-} \tag{1}$$

TABLE III

CHROMATOGRAPHIC RESULTS FOR VARIOUS TRIS(CHELATED) COMPLEXES ON A Λ-Ru-(phen)$_3{}^{2+}$–MONTMORILLONITE COLUMN

The separation factor is defined as in Table II. Maximum molecular rotations for Co(acac)$_2$(glycinate) and Cr(acac)$_2$(glycinate) were assumed to be $\pm$ 6000 (500 nm) and $\pm$ 3000 (485 nm), respectively.

Chelate amount (mole)	Initial (I) and final (F) eluents	Molecular rotation and wavelength (nm)	Resolution (%) and enantiomer in excess	Column size (cm × cm O.D.)	f_s
Co(acac)$_2$(glycinate) (2 · 10^{-5})	(I) Water (F) Water	$-$ 2500 (500) $+$ 4900 (500)	(Λ) (Δ)	1 × 1.2	1.5
Co(acac)$_2$(D,L-alaninate)	(I) Water (F) Water–methanol (2:1)	$-$ 3600 (485) $+$ 7200 (485)	80 (Λ) 100 (Δ)	1 × 1.2	2.0
Cr(acac)$_2$(glycinate) (1.5 · 10^{-5})	(I) Water (F) 0.1 M NaCl	$-$ 1500 (485) $+$ 1000 (485)	(Λ) (Δ)	2 × 1.2	1.2
Co(acac)$_2$(en)ClO$_4$ (1.5 · 10^{-5})	(I) Water (F) 0.1 M NaCl	$+$ 2400 (542)	47 (Δ)	0.5 × 1	
Co(acac)$_2$(NH$_3$)$_2$I (1.5 · 10^{-5})	(I) Water (F) 0.1 M NaCl	$+$ 1500 (545)	16 (Δ)	0.5 × 1	
Co(phen)(glycinate)$_2$Br (4 · 10^{-5})	(I) Water (F) 0.1 M NaCl	$+$ 450 (598)	33 (Λ)	0.5 × 1	

in which DH$_2$ and D denote the neutral and dianion forms of dimethylglyoxime. As seen from the figure, the exciton-split bands in Co(DH$_2$)$_3{}^{3+}$ shifted toward shorter wavelengths by about 15 nm compared with those of Co(DH)$_3$ and CoD$_3{}^{3-}$. This is reasonable because the π–π^* excitation in Co(DH$_2$)$_3{}^{3+}$ may require higher energy due to the stabilization of an electron in DH$_2$. The general trends of the CD curves did not change with the protonation and deprotonation of the complex. Since CoD$_3{}^{3-}$ has a tris(chelated) structure with symmetrical bidentate ligands, it was possible to apply the exciton-splitting theory to the positive and negative peaks below 300 nm in Fig. 2[21]. According to this theory, the effluent contained Λ-CoD$_3{}^{3-}$ as the enantiomer in excess. The configuration of Co(DH)$_3$ at neutral pH was assigned to Λ-fac-Co(DH)$_3$, because three protons were added to CoD$_3{}^{3-}$ in retaining the same configuration*.

The configuration of Co(DH)$_3$ was sustained for at least 200 h at room temperature without racemization. The situation was the same with CoD$_3{}^{3-}$. With Co(DH$_2$)$_3{}^{3+}$ it was not certain whether the complex racemized or not because it decomposed completely within 120 h at [HClO$_4$] = 1.0 M. According to eqn. 1, Co(DH)$_3$ has dual acid and base properties. In this respect, the resolved enantiomer could funmction as an acid–base catalyst with stereoselectivity.

Resolution of tris(1-nitroso-2-naphthol-3,6-disulphonato)cobalt(III)

The chemical species in a mixture of cobalt(II) ion and 1-nitroso-2-naphthol-

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* fac-Co(DH)$_3$ and CoD$_3{}^{3-}$ belong to the symmetry groups of C_{3v} and D_3, respectively. According to exciton-splitting theory[21] they should give the same type of CD curves.
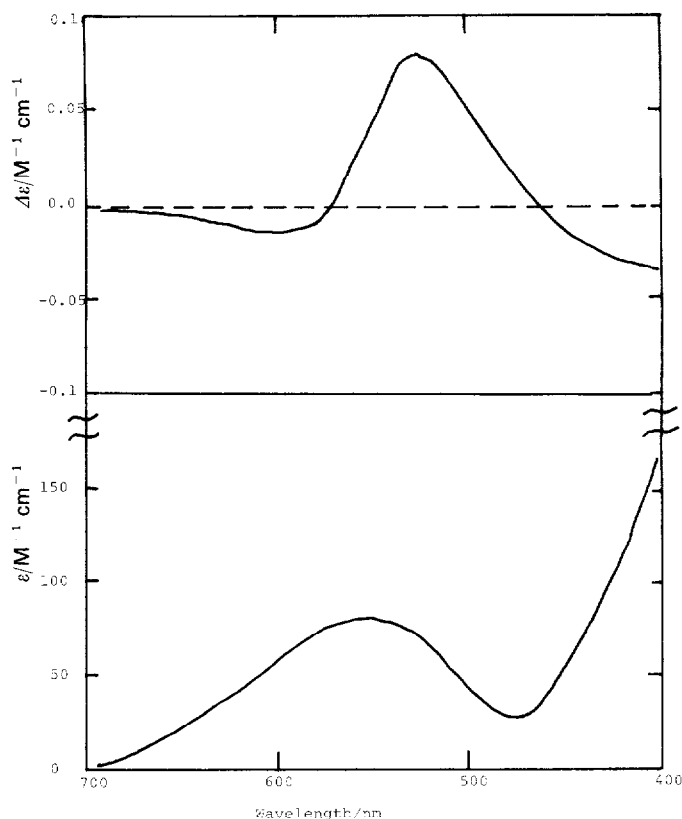
Fig. 1. The CD (upper) and electronic absorption (lower) spectra of the initial effluent for Cr(acac)$_2$(glycinate).

3,6-disulphonic acid had previously been identified as tris(1-nitroso-2-naphthol-3,6-disulphonato)cobaltate(III), Co(nitroso-R)$_3^{6-}$ (ref. 22). The complex carries six negative charges when all of the sulphonate groups are dissociated. Since anions are also adsorbed at the edges of montmorillonite[23], the negative chelate was expected to be resolved by the present column.

2.6 · 10^{-1} mole of Co(nitroso-R)$_3^{6-}$ in water were placed on a 2 × 1.2 cm O.D. Λ-Ru(phen)$_3^{2+}$–montmorillonite column. Prior to this, the column was eluted with 0.1 M ammonia aqueous solution. This is necessary in order to elute the chelate from the column with water. The chromatographic results are listed in Table V. Fig. 3 shows the CD curves of the effluents at 300–700 nm. As seen, there is no point at which ΔOD is zero, indicating that the effluents contained more than two kinds of optical isomers. When ΔOD at 650 and 380 nm is plotted against the elution volume, V, ΔOD changes in sign at around $V = 5$ and 13 ml, respectively. It is concluded that Co(nitroso-R)$_3^{6-}$ has two kinds of optical isomers, A and B; isomer A is eluted first with the initial enantiomer of curve 1, followed by isomer B with the final enantiomer of curve 8. Both curves consisted of two peaks with opposite signs. Since Co(nitroso-R)$_3^{6-}$ is a tris(bidentate) chelate of the type M(a–b)$_3$, it has *mer* and *fac* geometrical isomers. It is not

TABLE IV

CHROMATOGRAPHIC RESULTS FOR Co(DIMETHYLGLYOXIMATE)$_3$ ON A 2×1.2 cm O.D. Λ-Ru(phen)$_3^{2+}$–MONTMORILLONITE COLUMN

The eluent was water. Amount of chelate: $3 \cdot 10^{-5}$ mole.

Fraction No.	Volume (ml)	Concentration $(10^{-3}M)$	Molecular rotation at 467 nm and enantiomer in excess★,★★
1	6	4.60	+2020 (Δ)
2	3	3.04	−1810 (Λ)
3	3	0.82	−2800 (Λ)
4	3	0.34	−4110 (Λ)
5	3	0.21	−3300 (Λ)
6	3	0.14	−3500 (Λ)
7	3	0.30	−3100 (Λ)
8	3	0.075	−2500 (Λ)
9	3	0.055	−2300 (Λ)

★   The assignment was made from the CD spectra of the effluents (see text).

★★ Assuming that the maximum molecular rotation was ± 6000 at 467 nm, the retention volumes I and II and f_s (as defined in Table II) were calculated to be 3 ml, 5 ml and 1.7, respectively.

certain which of these isomers corresponds to the isomers A or B. However, it is deduced that the enantiomer of *fac* structure, which exhibited stronger affinity toward the column, had the CD curve with the negative and positive peaks at longer and shorter wavelengths, respectively, *i.e.*, the enantiomer has the Δ-configuration (see footnote on p. 46).

At pH = 5, the optical rotation of the effluents decreased gradually with a unimolecular rate constant of $1.9 \cdot 10^{-5}$ sec^{-1} at 20°C, indicating racemization of the complex. The details of the racemization mechanism are now under investigation.

Resolution of tris(catecholato)arsenate(V)

Tris(catecholato)arsenate(V) was placed on the same column as used in the precedent experiments. The complex was loaded as the potassium salt, KAs(cat)$_3$, and the chromatographic results are shown in Table VI. When the complex was eluted with water, only 70% of the initial amount was recovered. The effluents exhibited a positive optical rotation at 300 nm. The rest of the chelate was recovered by use of 0.1 M NH$_3$ aqueous solution. With this solvent, the effluents exhibited a negative angle of rotation. The molecular rotation at 300 nm, [M]$_{300}$, was +820 and −3200 for the initial and final effluents, respectively. Using the factor, [M]$_D$/[M]$_{300}$ = 0.11, obtained from the measured ORD curves, [M]$_D$ was calculated to be +74 and −290 for the initial and final effluents, respectively. Since Δ-As(cat)$_3$ and Λ-As(cat)$_3$ have [M]$_D$ of −21,000 and +21,000, respectively, the optical purities of the initial and final effluents were estimated to be 3.9% of Δ-As(cat)$_3^-$ and 15% of Λ-As(cat)$_3^-$, respectively[24]. In contrast with Co(nitroso-R)$_3^{6-}$, the Λ-isomer exibited the higher affinity toward the column.

Resolution of bis(chelated) cobalt complexes

So far the chelates investigated were restricted to tris(bidentate) chelates. It was also of interest to see whether a bis(terdentate) chelate was resolved on the present
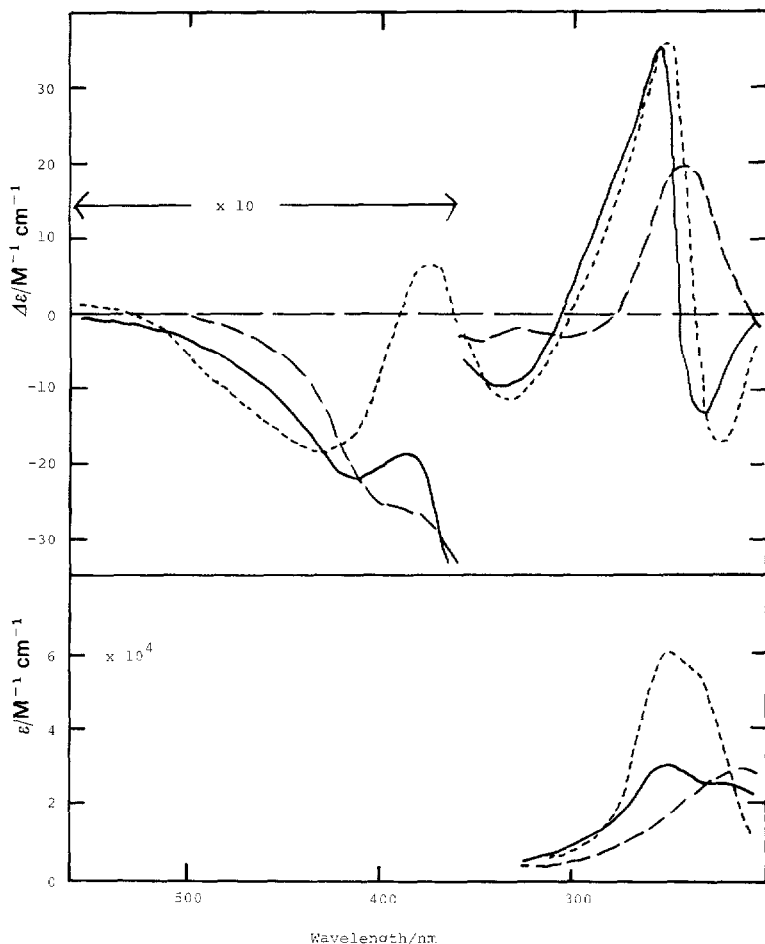
Fig. 2. The CD (upper) and electronic absorption (lower) spectra of partially resolved Co(dimethylglyoximate)$_3$; ———, neutral pH; ----, basic 0.1 M NaOH; – – –, acidic 0.1 M HClO$_4$.

type of column. It was not clear whether a tris(chelated) complex like Λ-Ru(phen)$_3^{2+}$ would interact stereoselectively with a bis(terdentate) chelate.

The chosen chelates were Co(II) and Co(III) complexes with terdentate pyridylazo-ligands. Since the ligands are linear, a pair of optical isomers exists as indicated in Fig. 4. The planar aromatic groups were expected to enhance the stereospecific stacking of a chelate with Λ-Ru(phen)$_3^{2+}$. In addition, the intense electronic absorption of these chelates in the visible region might help one to detect the occurrence of resolution.

7.5 · 10^{-7} mole of bis[4-(2-pyridylazo)resorcinol]cobalt(III) chloride, Co-(PAR)$_2$Cl, in water was placed on a 0.5 × 1.2 cm O.D. column. With water as eluent, the optical rotation in the effluent was as observed in Table VII. Fig. 5 shows the UV and CD spectra of the initial effluent. About 50% of the loaded chelate was separated. The rest could not be recovered with either 0.1 M sodium chloride or eth-

TABLE V.

CHROMATOGRAPHIC RESULTS FOR Co(NITROSO-R)$_3^{6-}$ ON A 2 × 1.2 cm O.D. Λ-Ru(phen)$_3^{2+}$– MONTMORILLONITE COLUMN

The eluent was water. The quantity of Co(nitroso-R)$_3^{6-}$ (nitroso-R = 1-nitroso-2-naphthol-3,6-disulphonate) was 2.6 · 10^{-6} mole. The column was pretreated with 0.1 M NH$_3$ aqueous solution. The retention volumes and separation factors were not estimated because the resolution of the present complex was complicated due to the presence of four kinds of optical isomers.

Fraction No.	Volume (ml)	Concentration (10^{-4} M)	ΔOD (× 10^{-4}) at 550 nm*	ΔOD (× 10^{-4}) at 380 nm*
1	1	0.46	+5.3	− 2.7
2	2	2.2	+8.0	−17.0
3	2	1.7	−0.7	−14.3
4	2	1.4	−3.4	− 8.8
5	2	2.6	−0.6	− 5.1
6	6	0.38	−0.5	+ 3.4
7	6	0.27	−0.4	+ 3.7
8	6	0.14	−0.2	+ 1.4
9	12	0.077	−0.0	+ 1.0

* The amplitude of the CD spectra at the indicated wavelength.

anol. The situation is similar to that observed for positively charged Co(phen)(glycinate)$_2^+$. As shown in Table VII, the water effluents always possessed negative [M]$_{480}$, implying that they contained either of the enantiomers of Co(PAR)$_2^+$ in excess.

Analogous results were obtained when bis[1-(2-pyridylazo)-2-naphthol]cobalt(III) chloride, Co(βPAN)$_2$Cl, was loaded on the column. In this case, however, resolution was achieved with ethanol as eluent, because no Co(βPAN)$_2^+$ was eluted with water. The chromatographic results are listed in Table VIII. Fig. 6 shows the UV and CD spectra of the initial effluent, and of Co(βPAN)$_2$ (dashed curve) prepared by reducing Co(βPAN)$_2^+$ with hydrazine hydrate.

The bis(chelated) complex of Co^{2+} with 2-(2-pyridylazo)-1-naphthol, Co(α-PAN)$_2$, was stable to oxidation by air for at least 30 min when prepared in ethanol. Thus, Co(αPAN)$_2$ in ethanol was loaded on the column and eluted with ethanol. The upper solid curve in Fig. 7 shows the CD spectrum of the initial 2-ml fraction; this changed gradually into the dashed curve. At this stage, the UV spectrum almost coincided with that of Co(αPAN)$_2^+$ in water. Thus, it is concluded that Co(αPAN)$_2$ was resolved partially on the present column and oxidized to Co(αPAN)$_2^+$ without changing its configuration. As far as is known, the resolution of Co(βPAN)$_2$ and Co(αPAN)$_2$ are the first examples to demonstrate that a terdentate Co(II) complex is stable to racemization.

1.0 · 10^{-6} mole of bis[2-(5-chloro-2-pyridylazo)-5-diethylaminophenolato]cobalt(III) chloride, Co(5-Cl-PADAP)$_2$Cl, in water was placed on a 0.5 × 1.2 cm O.D. column. No Co(III) chelate was eluted from the column by water. About 3.5% of the loaded chelate was obtained with 50 ml of ethanol as eluent. Fig. 8 shows the UV and CD spectra of the ethanol effluent. The CD curve consisted of a negative peak at longer wavelength (600 nm) and a positive one at shorter wavelength (570 nm). These features are opposite to those exhibited by the CD curves of the effluents of Co(PAR)$_2^+$, Co(βPAN)$_2^+$ and Co(αPAN)$_2$.
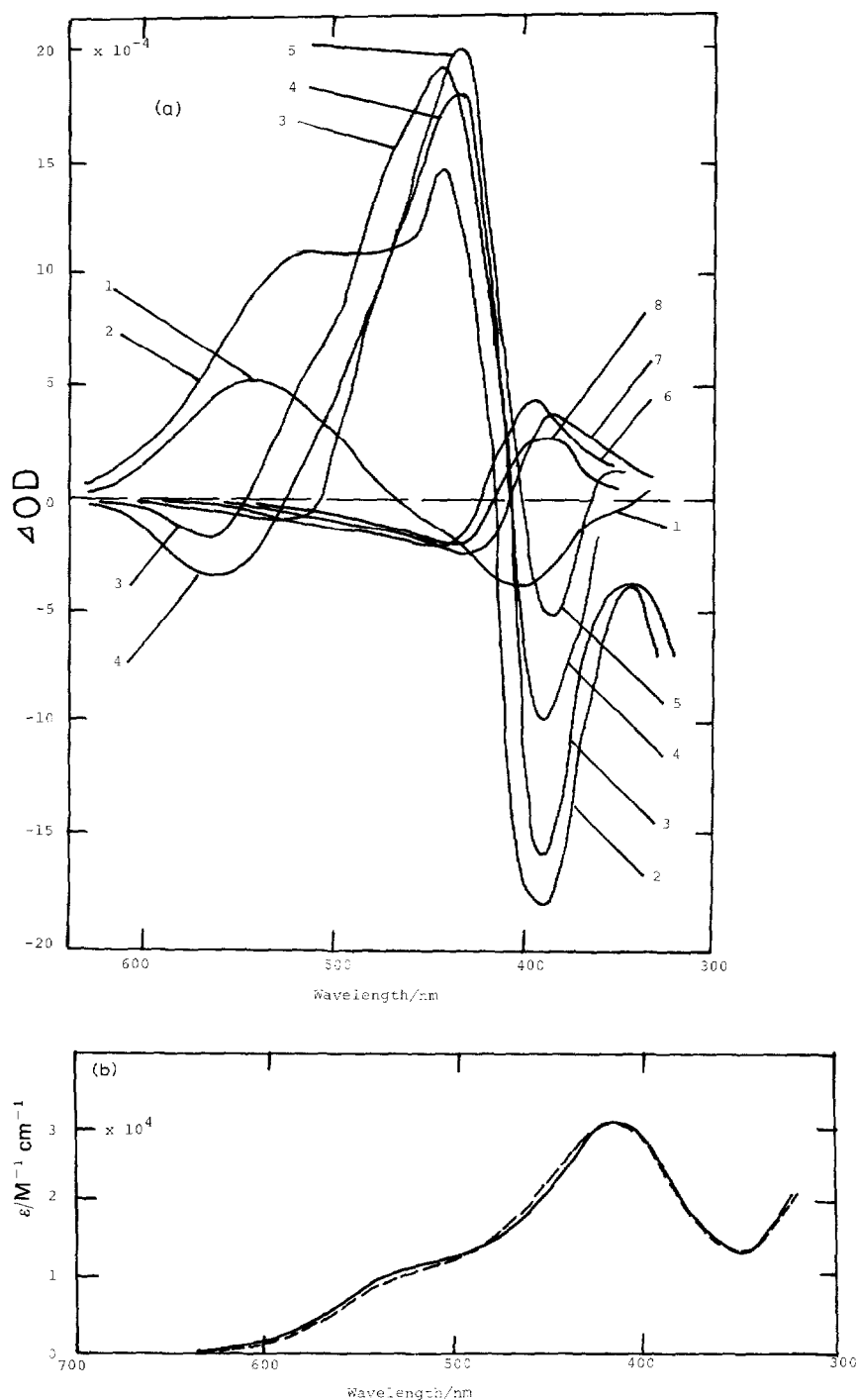
Fig. 3. (a) CD spectra of the effluents obtained in resolving Co(nitroso-R)$_3^{6-}$. The numbers on the curves correspond to those in Table V. (b) The electronic absorption spectra of fractions 1 (---) and 8 (———).

TABLE VI

CHROMATOGRAPHIC RESULTS FOR KAs(cat)$_3$ ON A 2 × 1.2 cm O.D. Λ-Ru(phen)$_3^{2+}$–MONTMORILLONITE COLUMN

The eluent was water for fractions 1–6 and 0.1 M NH$_3$ aqueous solution for fractions 7–10. The quantity of chelate, KAs(cat)$_3$ (cat = catecholate), was 7.3 · 10^{-5} mole.

Fraction No.	Volume (ml)	Concentration (10^{-4} M)	Molecular rotation at 300 nm	Resolution (%) and enantiomer in excess*,**
1	2	10.5	+820	3.9 (Δ)
2	2	12.5	+800	3.6 (Δ)
3	4	62.6	+330	1.6 (Δ)
4	4	35.2	+150	0.7 (Δ)
5	4	12.8	0	0
6	4	14.3	0	0
7	8	2.9	−1500	7.1 (Λ)
8	8	4.9	−2700	12 (Λ)
9	8	6.9	−3000	14 (Λ)
10	8	6.0	−3200	15 (Λ)

* Calculated on the basis of the molecular rotations of the Δ-and Λ-isomers being +21,000 and +21,000, respectively.

**Retention volumes I and II, and the separation factor, f_s (as defined in Table II) were 2.5 ml, 3.0 ml and 1.2, respectively. (Concentration peaks around 40 ml were neglected because the eluent was changed at the elution volume of 20 ml.)

Apparently the optical activity of these chelates is brought about by electronic coupling between the two coordinated ligands. Thus the CD spectra may be understood in terms of the exciton-splitting theory[21]. The transition moment of absorption around 500–600 nm in the present ligands is oriented from the pyridyl group to the phenyl or naphthyl groups[25], confirming that the absorption became optically active in the configurations of the isomers A and B in Fig. 4[21]. According to theoretical prediction, the CD curve of isomer B consists of one positive peak at longer wavelength and one negative peak at shorter wavelength. This is in accord with the CD spectra obtained for the initially eluted enantiomers, Figs. 5–7. It is noted here that isomer B is regarded as of configuration similar to that of the pseudo Δ-form of a tris(chelated) complex, when two N–N or N–O sites are occupied by two bidentate ligands. In this sense, the Δ-type isomers were eluted first for Co(PAR)$_2^+$, Co(βPAN)$_2^+$ and Co(αPAN)$_2$. In contrast, the CD curve of Co(5-Cl-PADAP)$_2^+$ exhibited opposite behaviour to the above three cases, indicating that the Λ-type isomer (or isomer A in Fig. 4) was eluted first.
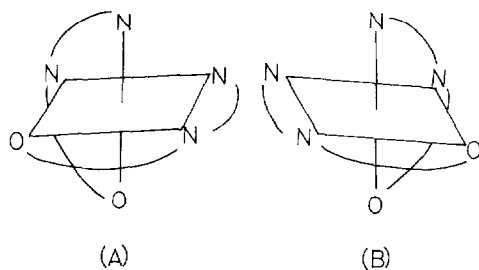

Fig. 4. The two optical isomers of a bis(terdentate) complex.

TABLE VII

CHROMATOGRAPHIC RESULTS FOR $Co(PAR)_2Cl$ ON A 0.5×1.2 cm Λ-Ru(phen)$_3^{2+}$–MONTMORILLONITE COLUMN

The eluent was water. The amount of chelate was $7.5 \cdot 10^{-7}$ mole. PAR = 4-(2-pyridylazo)resorcinol. The separation factor was not estimated because the second enantiomer was not eluted.

Fraction No.	Volume (ml)	Concentration $(10^{-5}M)$	Molecular rotation at 480 nm
1	2	3.9	−56,000
2	2	4.6	−26,000
3	5	1.9	− 5300
4	8	0.9	0
5	9	0.6	0

High-performance liquid chromatography

The trial for HPLC was performed using Λ-Ru(phen)$_3^{2+}$–montmorillonite as packing material (20 × 0.4 cm O.D.). The flow-rate of the eluent was 0.1 ml sec^{-1} under a pressure of 200–300 kg cm^{-2}. Fig. 9a–c shows the elution curves obtained when D,L-alanine, mer-Co(glycinate)$_3$ and a mixture of Co(acac)(glycinate)$_2$ and Co(acac)$_2$(glycinate) were charged in 0.1 ml of water. In all cases, the eluent was water. The effluent was collected every 1 ml and the UV and ORD spectra were recorded. No optical rotation was detected for the first two cases, indicating that D,L-alanine and mer-Co(glycinate)$_3$ were not resolved. In the third case, however, an optical rotation
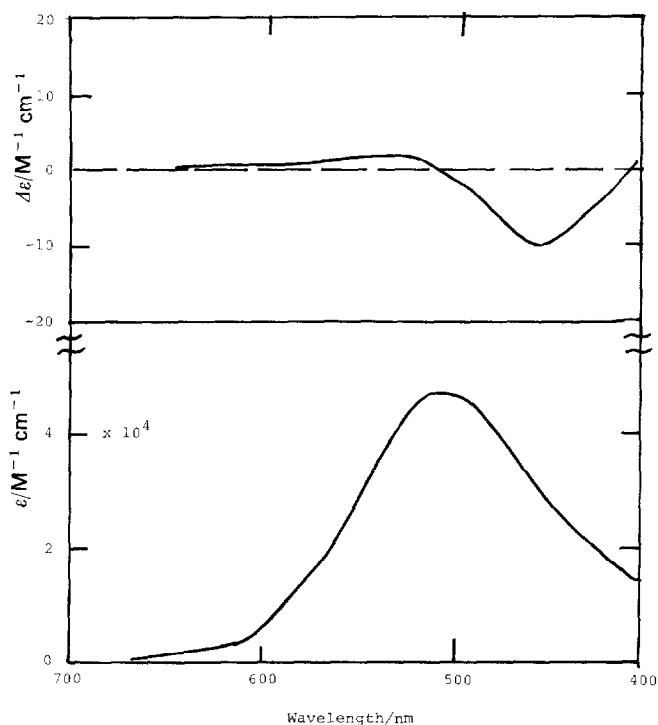

Fig. 5. The CD (upper) and electronic absorption (lower) spectra for the water effluent of $Co(PAR)_2^+$.

TABLE VIII

CHROMATOGRAPHIC RESULTS FOR Co(βPAN)$_2$Cl ON A 0.5 × 1.2 cm O.D. Λ-Ru(phen)Λ_2^{2+}–MONTMORILLONITE COLUMN

The eluent was ethanol. The amount of chelate was 3.5 · 10^{-7} mole. βPAN = 1-(2-pyridylazo)-2-naphthol.

Fraction No.	Volume (ml)	Concentration $(10^{-5}M)$	Molecular rotation at 600 nm
1	2	3.18	−47,000
2	2	2.24	−43,000
3	2	0.76	−10,500
4	2	0.67	0
5	6	0.36	0

at 480 nm appeared at an elution volume, V, of 1.5 ml and changed in sign from negative to positive around $V = 5$ ml. The peak in the UV spectra was shifted from 560 nm to 540 nm around $V = 1.5$ ml. The results imply that the first concentration peak at $V = 0.5$ ml corresponds to Co(acac)(glycinate)$_2$, while the second peak at $V = 2.3$ ml and the shoulder around $V = 6$ ml arise from Λ-Co(acac)$_2$(glycinate) and Δ-Co(acac)$_2$(glycinate), respectively. [M]$_{480}$ for the isomers were determined to be −2000 and +4500, respectively. The results are not very encouraging because the resolution efficiency for Co(acac)$_2$(glycinate) was not improved in comparison with that obtained on a 1 × 1.2 cm O.D. column (Table III).
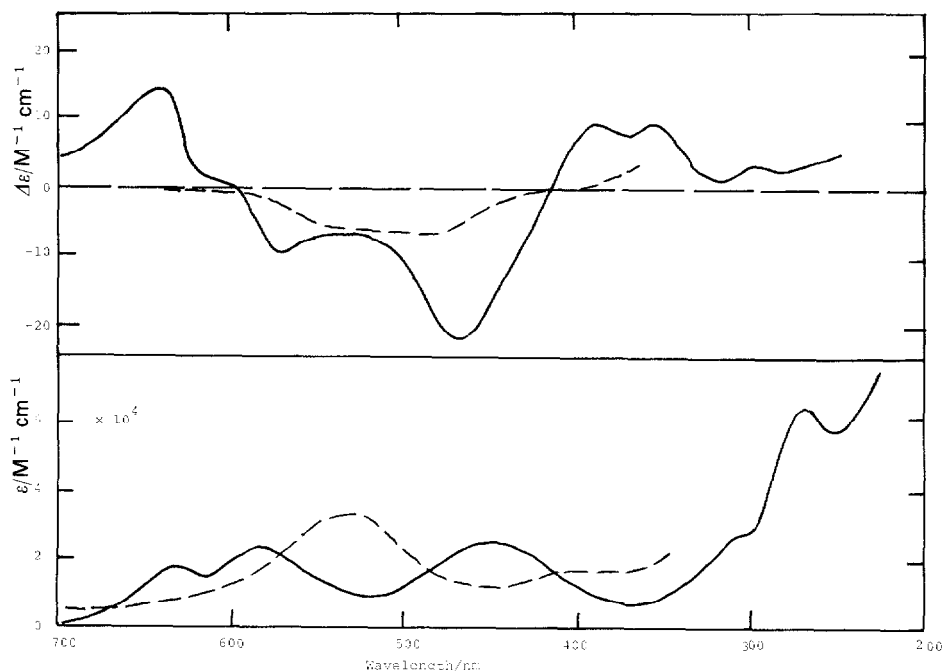

Fig. 6. The CD (upper) and electronic absorption (lower) spectra for the ethanol effluents of Co(βPAN)$_2^+$ (———) and Co(βPAN)$_2$ (---).
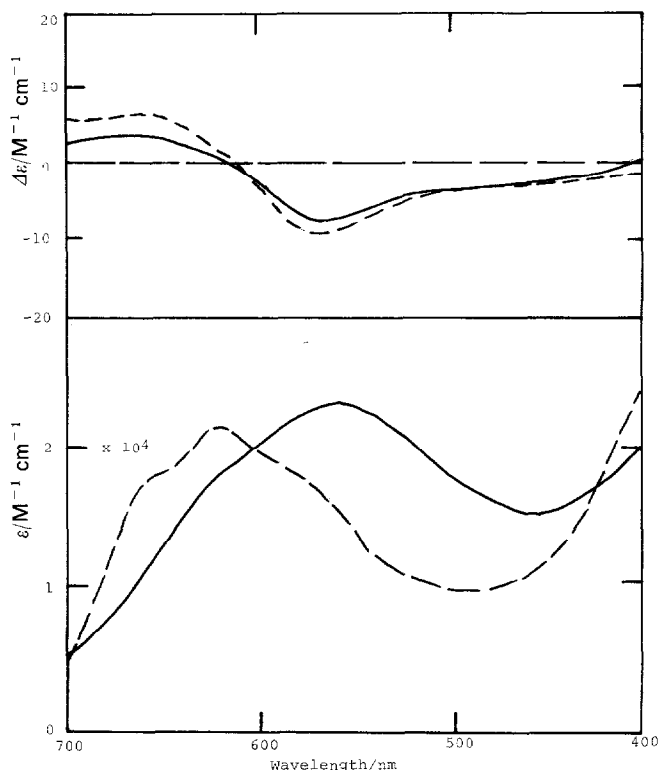
Fig. 7. The CD (upper) and electronic absorption (lower) spectra for the ethanol effluents of Co(αPAN)$_2$ (———) and Co(αPAN)$_2^+$ (---).

Chelates unresolved on a Λ-Ru(phen)$_3^{2+}$–montmorillonite column

The following tris- and bis(chelated) complexes were loaded on a 1–3 cm $\times$ 1.2 cm O.D. Λ-Ru(phen)$_3^{2+}$–montmorillonite column. When eluted with the solvents indicated in square brackets, they did not give any optical rotation (< 0.01 ˚ cm^{-1}) in the whole effluent: Al(8-quinolinolate)$_3$ [CHCl$_3$]; Co(en)(glycinate)$_2$Br [water]; Cu(D,L-alaninate)$_2$ [water]; mer-Co(glycinate)$_3$ [water]; Zn(8-hydroxyquinoline-5-sulphonate)$_2$ [10^{-3} M NaOH]. Thus these chelates were not resolved on the present column.

Chromatography on other kinds of adsorbents

In order to compare the performance of the present clay column, other kinds of ion-exchangers were used to preadsorb optically active Ru(phen)$_3^{2+}$.

First a cation-exchange resin (Dowex 50-X8) was tried. Δ-Ru(phen)$_3$Cl$_2$ in water was loaded on a 6 $\times$ 1.2 cm O.D. column of the cation-exchange resin (Na$^+$). Only 20% of the whole cation-exchange sites in the resin (3 $\cdot$ 10^{-3} equiv.) were replaced by Δ-Ru(phen)$_3^{2+}$, and preadsorbed Δ-Ru(phen)$_3^{2+}$ was gradually separated by water. Thus the cation-exchange resin could not be used as an adsorbent for the present type of chromatography, because its binding of Δ-Ru(phen)$_3^{2+}$ is too weak.

Next SP-Sephadex C-25 was used as an adsorbent. When Δ-Ru(phen)$_3$Cl$_2$ was loaded on a 1 $\times$ 1.2 cm O.D. column Na$^+$ ions at all the cation-exchange sites were
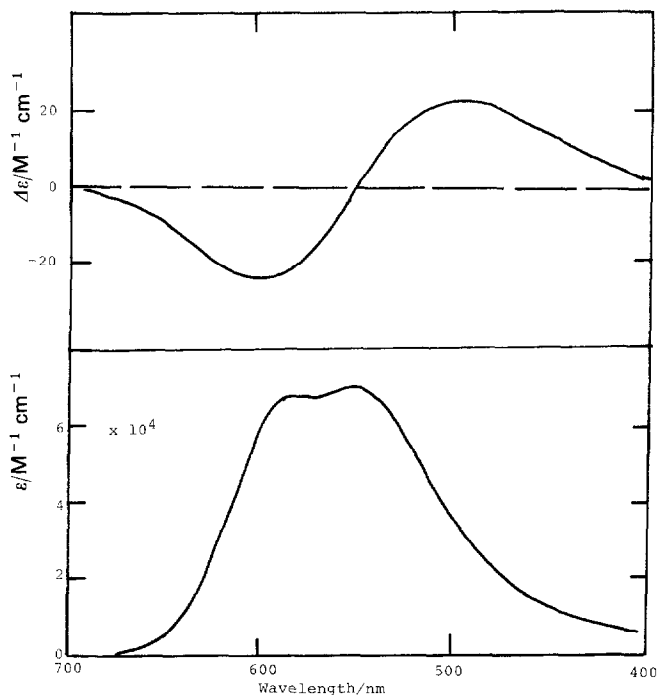
Fig. 8. The CD (upper) and electronic absorption (lower) spectra for the ethanol effluents of Co(5-Cl-PA-DAP)$_2^+$.

replaced by Δ-Ru(phen)$_3^{2+}$. In this case, no Δ-Ru(phen)$_3^{2+}$ was eluted by water. $2 \cdot 10^{-6}$ mole of Co(acac)$_3$ were placed on the column and eluted with water. All the Co(acac)$_3$ was recovered with 5 ml of water, and no optical rotation was exhibited by the effluent collected at every 1 ml. Thus Δ-Ru(phen)$_3^{2+}$–SP-Sephadex C-25 was unable to resolve Co(acac)$_3$.

Finally Λ-Co(phen)$_2$(L-valinate)$^{2+}$–montmorillonite was used as a column material. $2.2 \cdot 10^{-6}$ mole of Co(acac)$_3$ in water were placed on the column and eluted with water. The initial effluent fraction of 2 ml contained $2.6 \cdot 10^{-4}$ M Co(acac)$_3$ and exhibited a molecular rotation at 480 nm of $[M]_{480} = 2000$. The second and third fractions of 2 ml contained $5.3 \cdot 10^{-4}$ M and $3.3 \cdot 10^{-4}$ M of Co(acac)$_3$ with $[M]_{480} = +400$ and -800, respectively. Thus, Δ-Co(acac)$_3$ was eluted first with an optical purity of 6.6%. The efficiency of resolution was much lower than that of a Λ–Ru(phen)$_3^{2+}$–montmorillonite column (Tables I and II). The reason may lie in the fact that Λ-Co(phen)$_2$(L-valinate)$^{2+}$ has two 1,10-phenanthroline ligands, whereas Λ-Ru(phen)$_3^{2+}$ has three such ligands. This results in a lower stereospecificity in the molecular stacking of Co(acac)$_3$ with the preadsorbed metal chelates.

X-Ray diffraction measurements

The basal spacing, $d(001)$, of solid Λ-Ru(phen)$_3^{2+}$–montmorillonite was measured by X-ray diffraction under various conditions. It was calculated from the smallest diffraction angle, θ, according to $d(001) \sin 2\theta = \lambda$, with $\lambda = 1.542$ Å. $d(001)$ was
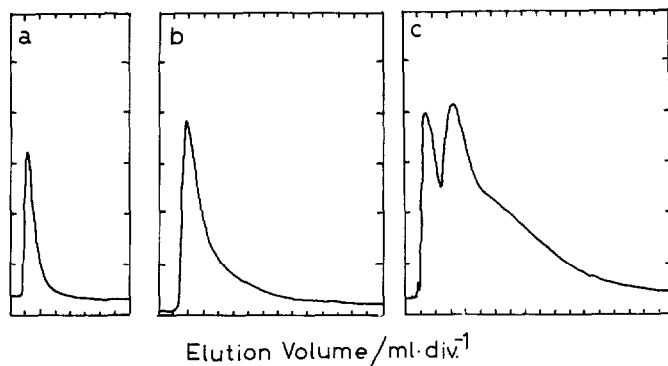
Fig. 9. HPLC elution curves on Λ-Ru(phen)$_3$$^{2+}$–montmorillonite; a, D,L-alanine; b, *mer*-Co(glycinate)$_3$; c, a mixture of Co(acac)(glycinate)$_2$ and Co(acac)$_2$(glycinate).

determined to be 18.8 ± 0.2 Å for the dry sample. No diffraction was observed at the angle which gave the $d(001)$ ($= 12.3$ Å) for dry sodium montmorillonite. The results confirm the intercalation of Λ-Ru(phen)$_3$$^{2+}$ in the interlayer space of the whole clay. No increase in $d(001)$ was observed when the dry sample (10 mg) was soaked in either 10 ml of water or methanol, both containing $1 \cdot 10^{-3}$ M Co(acac)$_3$. Thus there was no evidence for the penetration of either solvent or Co(acac)$_3$ into the interlayer space.

TABLE IX

CHROMATOGRAPHIC RESULTS ON A Λ-Ru(phen)$_3$$^{2+}$–MONTMORILLONITE COLUMN

The preferred enantiomer for a bis(terdentate) chelate is indicated according to Λ and Δ for structures A and B respectively in Fig. 4.

Chelate	Initial eluent	Preferred enantiomer
Co(acac)$_3$	Water	Δ
Co(acac)$_3$	Water–methanol (2:1)	Λ
Cr(acac)$_3$	Water–methanol (2:1)	Λ
Cr(acac)$_3$	95% Methanol	Λ
Cr(acac)$_3$	Chloroform	Λ
Rh(acac)$_3$	Water–methanol (2:1)	Λ
Cr(3-nitroacetylacetonate)$_3$	Chloroform	Δ
Co(acac)$_2$(glycinate)	Water	Δ
Co(acac)$_2$(D,L-alaninate)	Water	Δ
Cr(acac)$_2$(en)$^+$	Water	Λ
Co(acac)$_2$(NH$_3$)$_2$$^+$	Water	Λ
Co(phen)(glycinate)$_2$$^+$	Water	Δ
Co(dimethylglyoximate)$_3$	Water	Λ
Co(nitroso-R)$_3$$^{6-}$	Water	Δ
As(catecholate)$_3$$^-$	Water	Λ
Co(PAR)$_2$$^-$	Water	Λ
Co(βPAN)$_2$$^+$	Ethanol	Λ
Co(αPAN)$_2$	Ethanol	Λ
Co(5-Cl-PADAP)$_2$$^+$	Ethanol	Δ

DISCUSSION

Table IX summarizes the chromatographic results for the complexes which were resolved on a Λ-Ru(phen)$_3{}^{2+}$–montmorillonite column. The column of "preferred enantiomer" denotes the configuration of the enantiomer which exhibited higher affinity toward the column.

From the practical point of view, chromatography on the present column is distinguished from the known methods in two respects, high resolution efficiency and wide applicability. As for the first point, the results for Co(acac)$_3$ have already been compared with the performance of a SP-Sephadex C-25 column. As for the second point, no single column has resolved all of the neutral, positively and negatively charged complexes by use of pure solvents or their mixtures. In the case of Sephadex ion-exchangers, for example, optically active substances should be added to the eluent, depending on the kinds of chelates to be resolved[26].

At present, no complete picture for resolution mechanisms can be deduced from the rather phenomenological information at hand. A few points, however, can be made concerning the structures of the binding sites. First, in the case of Co(acac)$_3$, the Λ-isomer was eluted first followed by the Δ-isomer when water was used as eluent. This order was reversed when water–methanol (2:1) was employed. Such a reversal is difficult to interpret in terms of competitive adsorption between Λ- and Δ-isomers (Λ-M and Δ-M) onto identical binding sites, [S]:

$$\Lambda\text{-M} + [\text{S}] \rightleftharpoons \Lambda\text{-M/[S]} \tag{2}$$

$$\Delta\text{-M} + [\text{S}] \rightleftharpoons \Delta\text{-M/[S]} \tag{3}$$

Apparently the difference in the solvation structures of Co(acac)$_3$ in water and in water–methanol solvents has no influence on the relative positions of equilibria 2 and 3, since the solvents used are achiral. Thus, the observed reversal in chirality recognition is induced only when solvent molecules are incorporated in the structures in such a way that Δ-M/[S] is stabilized in water, while the opposite situation pertains in water–methanol. It is unlikely, however, that such a specific interaction is operative between the present solvent molecules and Co(acac)$_3$, which has no functional groups capable of interacting with the solvent molecules.

The above solvent effects are interpreted more reasonably if the Λ- and Δ-isomers are adsorbed independently on different binding sites:

$$\Lambda\text{-M} + \Lambda\text{-[S]} \rightleftharpoons \Lambda\text{-M/}\Lambda\text{-[S]} \tag{4}$$

$$\Delta\text{-M} + \Delta\text{-[S]} \rightleftharpoons \Delta\text{-M/}\Delta\text{-[S]} \tag{5}$$

Based on molecular models, it was previously suggested that Λ-[S] and Δ-[S] comprised the spaces over the head of and by the side of preadsorbed Λ-Ru(phen)$_3{}^{2+}$, respectively. There is no empty space over the head of Λ-Ru(phen)$_3{}^{2+}$ intercalated between clay sheets. Thus, Λ-[S] exists only on the external surface of the solid. On the other hand, the space adjacent to Λ-Ru(phen)$_3{}^{2+}$ is accessible for a chelate in both interlayer and external regions. Thus, Δ-[S] exists both inside the interlayer space and

on the external surface. We recall here the fact that water molecules are a much stronger adsorbate than methanol molecules toward a clay[27]. Accordingly, it is not unreasonable to expect that Δ-Co(acac)$_3$ solvated by water molecules is capable of approaching Δ-[S] inside the interlayer space, while the same isomer solvated by methanol molecules is unable to penetrate the interlayer space. Under these conditions, eqn. 4 is applicable in water–methanol while eqn. 5 is applicable in water, if Λ-Co(acac)$_3$ is more strongly adsorbed at Λ-[S] than Δ-Co(acac)$_3$ is at Δ-[S] in the former solvent.

Based on the above considerations, the following conclusions may be drawn about the preference of a resolved chelate. (i) A chelate which has affinity toward a clay surface may show a tendency for its Δ-isomer to be bound to the column more firmly than its Λ-isomer. This is because Δ-M/Δ-[S] is more stabilized than Λ-M/Λ-[S] due to the attractive interaction of Δ-M with the clay. (ii) A chelate which has little affinity toward or repulsive interaction with a clay may show a tendency for its Λ-isomer will be bound to the column more firmly. Λ-M/Λ-[S] is more stabilized than Δ-M/Δ-[S] because the former is more distant from a clay surface than is the latter. (iii) For a chelate which is too bulky to penetrate the interlayer space or solvated by solvent molecules inert to a clay, only the sites on the external surface are accessible. Which of Λ-M/Λ-[S] and Δ-M/Δ-[S] is the more stabilized may depend on the properties of the chelate.

The Λ-isomers were preferred in the cases of Co(acac)$_3$ and Rh(acac)$_3$ when water–methanol, methanol and chloroform were used as eluents. This may be rationalized according to (ii) and (iii), i.e., these chelates do not penetrate the interlayer space in the solvents used and have no affinity toward the clay. In contrast, the Δ-isomers of Co(acac)$_2$(glycinate), Co(acac)$_2$(D,L-alaninate) and Cr(acac)$_2$(glycinate) were preferred in water as eluent. This was probably because the interaction of a coordinated amino acid with a clay stabilizes Δ-M/Δ-[S] both inside the interlayer space and on the external surface (i).

In contrast to Cr(acac)$_3$, the Δ-isomer of Cr(3-nitroacetylacetonate)$_3$ is preferred by the column even in chloroform as eluent. Most probably, hydrogen bonding of the nitro group in the chelate with the hydroxyl groups of the clay results in stabilization of Δ-M/Δ-[S] (i). Such hydrogen bonding does not occur for Λ-M/Λ-[S] since in this case the isomer is too distant from the surface of the clay.

According to (i), positively charged chelates are expected to show the racemic preference, because the electrostatic attraction to the negative charge in the clay stabilizes the Δ-isomer at Δ-[S] to a greater degree than the Λ-isomer at Λ-[S]. The opposite tendency is expected for a negatively charged chelate due to the repulsive interaction with the clay (ii). The racemic preference of Co(phen)(glycinate)$_2^+$ and the enantiomeric preference of As(cat)$_3^-$ toward the column are in accord with this expectation. On the other hand, the enantiomeric preference of Co(acac)$_2$(en)$^+$ and Co(acac)$_2$(NH$_3$)$_2^+$ and the racemic preference of Co(nitroso-R)$_3^{6-}$ are not in accord with the above expectations. The results indicate that interaction other than electrostatic is operating between these chelates and the clay. In the case of Co(nitroso-R)$_3^{6-}$, for example, the coordination of the sulphonate groups in the chelate with an Al^{3+} at the edge of the clay may enhance the affinity of the chelate toward the clay.

For Co(βPAN)$_2^+$, Co(αPAN)$_2$ and Co(5-Cl-PADAP)$_2^+$, only the sites on the external surface are accessible, because these chelates are too bulky to penetrate the interlayer space (iii). If these bis(terdentate) chelates are regarded as two-bladed pro-

pellers with Λ- or Δ-configurations, the first two show the enantiomeric preference while the last shows the racemic one. The results indicate that the mode of stacking of these chelates with Λ-Ru(phen)$_3^{2+}$ is determined by a very delicate balance between various interactions. No clear model is available at present. The resolution of these bis(terdentate) chelates may reveal a new series of examples for studying the applicability of the exciton splitting theory.

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