Chirality Recognition of a Clay Surface modified by an Optically Active Metal Chelate

Akihiko Yamagishi
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Using Δ-tris(1,10-phenanthroline)nickel(II) montmorillonite as a column material, the chromatographic behaviour of ten Co^{III} chelates of the type $[Co(acac)_2(L)]$ (acac = acetylacetonate; HL = α-amino-acid) have been compared. All of the chelates were resolved at least partially into two configurational isomers. Which of the isomers was bound with the column more firmly depended on the nature of the side-chain in the amino-acid. The results indicate that the modified clay surface recognized the chirality of an adsorbate very distinctly.

Resolution by stereoselective adsorption on an optically active solid surface is often thought to be related to the origin of chirality in living systems.[1] The possibility of such resolution is well known, but the results are controversial. For example, several investigators observed the optical rotation in an eluant when racemates were passed through a column of optically active quartz.[2] In some cases, however, scattering by small particles was responsible for the observed optical rotation.[3] Similar arguments apply concerning the adsorption on a clay. The occurrence of stereospecific adsorption or activation of molecules was also claimed in the presence of a colloidal clay.[4] Most of the results, however, were denied by later experiments which were performed under more rigorous conditions.[5] There exist few unequivocal cases of resolution on an inorganic solid which owes its chirality to crystal packing rather than to molecular asymmetry.[6]

In contrast to the above situations, it was recently revealed that a clay could discriminate the chirality of an approaching molecule, if it was modified by an optically active molecule.[7] For example, the Λ-isomer of tris(1,10-phenanthroline)-iron(II), Λ-$[Fe(phen)_3]^{2+}$, was preferentially adsorbed on a Δ-$[Ni(phen)_3]^{2+}$ montmorillonite.[7c] Such selectivity arose from the tendency of an optically active complex to pair with its optical antipode on the silicate sheet of a montmorillonite. In the above example, Λ-$[Fe(phen)_3]^{2+}$ prefers Δ-$[Ni(phen)_3]^{2+}$ as a stacking partner, even if the paired chelates are of a different type. Based on the molecular model, Λ- and Δ-isomers were suspected to be stacked in an alternative way inside the interlayer space.

The above observation gives some clues as to the origin and development of chirality in biological systems. That is, once an optically active chelate is generated in nature, the produced enantiomer can resolve another kind of chelate being adsorbed on a clay surface. The scheme of resolution in equation (1) is assumed, in which Δ-M^1 denotes an optically active

$$\Delta\text{-M}^1\cdot\text{clay} + \text{rac}\cdot\text{M}^2 \longrightarrow \Delta\text{-M}^1\cdot\Lambda\text{-M}^2\cdot\text{clay} + \Delta\text{-M}^2 \quad (1)$$

complex and rac·M^2 a racemic mixture of a different kind. In this scheme, the clay plays the role of a medium copying the molecular asymmetry from one kind of molecule (M^1) to another (M^2). Allowing such a resolution mechanism on a global scale, the hypothesis is introduced that, during the chemical evolution, there existed a chain, transferring molecular asymmetry from one molecule to another on a clay surface until the chirality was finally present in the amino-acids or glucose as seen in the present forms of biological systems.

In order to validate the above hypothesis, it is of vital importance to establish the relation between the type of modification of the clay surface and the latter's ability for chirality recognition. In the present paper, we attacked this problem by the method of column chromatography, using a clay as a column material. The chromatographic behaviour was compared among a series of cobalt(III) chelates of the type $[Co(acac)_2(L)]$ (acac = acetylacetonate; HL = α-amino-acid). These chelates were placed on a column of Δ-$[Ni(phen)_3]^{2+}$ montmorillonite. Attention was focused on how sensitive the chirality recognition by the column was to changes in the structure of the resolved chelate

Table 1. Chromatographic results for $[Co(acac)_2(\text{DL-AlaO})]$ on a Δ-$[Ni(phen)_3]^{2+}$ montmorillonite column

Expt. no.^{a}	Volume (cm^3)	10^3 C ^{b}/ mol dm^{-3}	o.r. at 500 nm ^{c}/° cm^{-1}	$[M]_{500}$ ^{d}
1	8.0	0	0.000	0
2	8.0	1.66	0.094	5 700
3	8.0	1.63	0.070	4 300
4	8.0	1.47	0.044	3 000
5	8.0	1.28	0.020	1 600
6	8.0	1.06	−0.008	−800
7	8.0	0.84	−0.010	−1 300
8	8.0	0.50	−0.010	−2 000
9	8.0	0.34	−0.010	−2 900
10	32.0	0.72	−0.038	−5 300

^{a} Eluting solvent was water for experiments 1—9 or methanol for experiment 10. ^{b} Concentration of chelate. ^{c} o.r. = Optical rotation. ^{d} Molecular rotation at 500 nm.

Experimental

Δ-$[Ni(phen)_3]^{2+}$ montmorillonite was prepared by adding Δ-$[Ni(phen)_3]Cl_2$ to an aqueous solution of colloidally dispersed sodium montmorillonite (Na^+M^-). The replacement of the counter cation in Na^+M^- with Δ-$[Ni(phen)_3]^{2+}$ occurred completely in the stoicheiometric conditions. That is, Δ-$[Ni(phen)_3]^{2+}$ occupied two cation-exchange sites per chelate. The mixture was centrifuged and the supernatant was decanted. The precipitate was washed with methanol and dried under vacuum. A slurry of Δ-$[Ni(phen)_3]^{2+}$ montmorillonite (5 g) in water was poured over a 3G3 glass filter to form a 1 cm × 3 cm outside diameter column. The interstitial volume of the column was determined to be 2 cm^3. The flow rate of the eluting solvent was 0.03 cm^3 min^{-1}. The following procedures were carried out at 2 °C at which temperature the racemization of preadsorbed Δ-$[Ni(phen)_3]^{2+}$ was negligible.

$[Co(acac)_2(L)]$ was prepared according to the literature,[8] where HL = amino-acid as listed in Table 2. The compounds were identified by their i.r. and electronic spectra.[8]

The electronic spectra of the effluents were measured with a

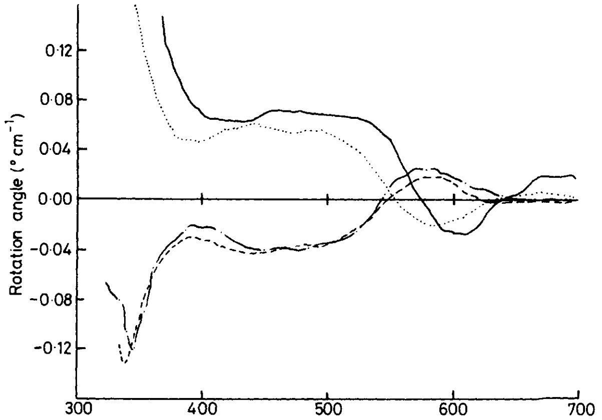


Figure 1. The o.r.d. curves of the last effluents of $[Co(acac)_2(L)]$: L = DL-AlaO (— — —), DL-ProO (— · — · —), and DL-PheO (· · · ·); and of $[Co(acac)_3]$ (——)

EPS-3T spectrophotometer. The optical rotatory dispersion (o.r.d.) spectra were recorded with a JEOL UV/ORD-5 spectrophotometer.

Results

$[Co(acac)_2(L)]$ solution (5 cm^3 of *ca.* 10^{-3} mol dm^{-3}) was placed on the column and first eluted with water. The concentration of recovered chelate in each effluent was measured spectrophotometrically (ε = 150—200 at 560—570 nm).[8] Elution was continued until the concentration of the eluted cobalt chelate became less than 4×10^{-4} mol dm^{-3}. After this stage, the solvent used was methanol in order to recover the rest of the original chelate. The present neutral chelates dissolved more easily in methanol than in water. The efficiency of resolution was examined by measuring the o.r.d. curves of the effluents at 350—700 nm.

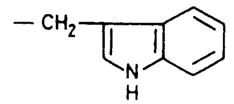
An example of the chromatographic results is shown in Table 1 for $[Co(acac)_2(DL\text{-}AlaO)]$ (AlaO = alaninate). More than half of the initial chelate was recovered by eluting water. During this stage, the optical rotation at 500 nm appeared and its sign was inverted from the initial value, indicating that the configuration of an excess enantiomer had changed. When about 70 cm^3 of water had been passed down the column, the concentration of the chelate became less than 4×10^{-4} mol dm^{-3}. The rest of the original chelate was recovered with methanol. The optical rotation of the methanol effluents had a constant sign.

The other cobalt chelates were resolved similarly to $[Co(acac)_2(DL\text{-}AlaO)]$ except for L = DL-prolinate (DL-ProO), DL-phenylalaninate (DL-PheO), DL-tryptophanate (DL-TrpO), and DL-methioninate (DL-MetO). The latter class of the chelates was not recovered with water to a measurable extent. Therefore, the chromatogram was obtained using water–methanol (4 : 1 v/v) as an initial solvent. With this mixed solvent, the whole of the original chelate was recovered, changing the sign of the optical rotation at 500 nm.

As shown in Figure 1, the o.r.d. curves of the resolved chelates show a large Cotton effect around 550 nm. By comparing the curves with that of the enantiomer of $[Co(acac)_3]$, it can be concluded that the positive or negative optical rotation at 500 nm corresponds to the pseudo Δ- or Λ-isomer, respectively. This assignment coincides with the conclusions derived by *X*-ray crystallography.[9]

Table 2 lists the configuration of the excess enantiomer in the last fraction, or the enantiomer showing the higher affinity toward the Δ-$[Ni(phen)_3]^{2+}$ montmorillonite. The Table also includes the molecular rotation at 500 nm, $[M]_{500}$, for the enantiomer; it was considered to be the lower limit of the real value. The results for $[Co(acac)_3]$ and $[Co(acac)_2(GlyO)]$ (GlyO = glycinate) on the same column are also included in Table 2.

Table 2. Resolution of $[Co(acac)_2(L)]$ on a Δ-$[Ni(phen)_3]^{2+}$ montmorillonite column



(A)

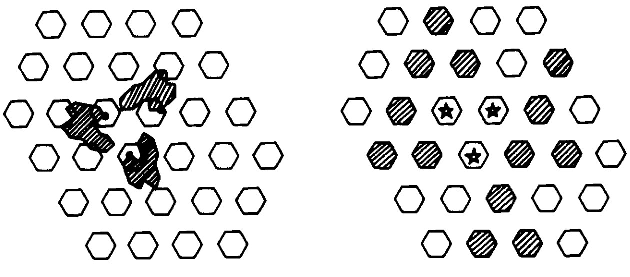
L	Side-chain structure	Preferred enantiomer [a]	$[M]_{500}$
GlyO	$-H$	Λ	−11 000
AlaO	$-CH_3$	Λ	−5 300
ValO [b]	$-CH(CH_3)_2$	Δ	+1 100
LeuO [c]	$-CH_2CH(CH_3)_2$	Δ	+600
SerO [d]	$-CH_2OH$	Λ	−3 100
ThreO [e]	$-CH(OH)CH_3$	Δ	+5 300
ProO	$-CH_2CH_2CH_2-$	Λ	−940
MetO	$-CH_2CH_2SCH_3$	Δ	+7 300
PheO	$-CH_2Ph$	Δ	+4 900
TrpO	(A)	Λ	−5 900
acac		Δ	+24 000

[a] The configuration of an enantiomer bound to the column more firmly than its optical antipode. [b] Valinate. [c] Leucinate. [d] Serinate. [e] Threoninate.

Discussion

The investigated chelates can be divided into two groups. Group I contains the chelates whose Λ-isomers are preferred by the column {racemic preference with respect to preadsorbed Δ-$[Ni(phen)_3]^{2+}$}, while group II involves the chelates whose Δ-isomers are preferred by the column (enantiomeric preference). The distinction between these two groups appears to lie in the structure of the side-chain of a co-ordinated amino-acid. That is, an amino-acid in a group I chelate has only one primary carbon atom or less in its side-chain, while an amino-acid in a group II chelate has either more than two primary carbon atoms or branched carbon atoms. The exceptions to the above rule are ProO and TrpO chelates. These chelates belong to group I, although the former has three carbon atoms and the latter an indole ring in the side-chains of their amino-acids.

A silicate sheet in a montmorillonite layer consists of a two-dimensional lattice of tetrahedral rings [Figure 2(*a*)].[10] From the electric dichroism measurements, an adsorbed $[Fe(phen)_3]^{2+}$ ion was found to orientate its C_3 axis perpendicularly to the surface.[11] Accordingly, $[Ni(phen)_3]^{2+}$ may also be adsorbed in the same conformation in the present column. When $[Ni(phen)_3]^{2+}$ was adsorbed at the saturated amount of cation-exchange capacity of montmorillonite, each Ni chelate occupied three tetrahedral rings as shown in Figure 2(*b*). In the Figure, a shaded ring denotes the one occupied by a phenanthroline ligand in Δ-$[Ni(phen)_3]^{2+}$. In such situations, there are two different binding sites conceivable for an eluted chelate. One is by the side of Δ-$[Ni(phen)_3]^{2+}$ and the other over the head of Δ-$[Ni(phen)_3]^{2+}$ [Figure 2(*b*)]. If an eluted molecule is a pseudo-tris-chelated complex as in the present case, the molecular stacking model predicts that the pseudo Λ-isomer is preferred at the position adjacent to Δ-



(a) (b)

Figure 2. (*a*) Schematic drawing of a silicate sheet of montmorillonite. A hexagon denotes a tetrahedral ring surrounded by six SiO_4^{4-} tetrahedra; three shaded wings are phen ligands in $[Ni(phen)_3]^{2+}$. (*b*) Two possible binding sites on a Δ-$[Ni(phen)_3]^{2+}$ montmorillonite surface. The shaded hexagons denote the tetrahedral rings occupied by the Ni^{II} chelate; the site denoted by three stars is a racemic binding site by the side of Δ-$[Ni(phen)_3]^{2+}$ and that over the head of the $[Ni(phen)_3]^{2+}$ ion is an enantiomeric site

$[Ni(phen)_3]^{2+}$. Contrary to this, the pseudo Λ-isomer is preferred over the head of Δ-$[Ni(phen)_3]^{2+}$.

Which of the above sites the chelate prefers depends on its properties. If a chelate has an affinity toward the silicate sheet, it may take a position by the side of Δ-$[Ni(phen)_3]^{2+}$ in order to be as close to the surface as possible. On the other hand, if a chelate has an affinity toward the phen ligands, it will be located over the head of Δ-$[Ni(phen)_3]^{2+}$. This prediction is reasonable on the basis of the following facts: that is, $[Fe(phen)_3]^{2+}$, a strong adsorbate on sodium montmorillonite, stacks with Δ-$[Ni(phen)_3]^{2+}$ as a racemic pair, while $[Ru(acac)_3]$, which does not interact with sodium montmorillonite in the absence of Δ-$[Ni(phen)_3]^{2+}$, stacks with Δ-$[Ni(phen)_3]^{2+}$ as an enantiomeric pair.[7]

Based on the above postulates, the structural character of a group II chelate may be rationalized in terms of the fact that such branching or aromatic properties on a side-chain increases the affinity toward the aromatic planes of phen ligands. The bulkiness of the side-chain may make it difficult for a group II chelate to be located in the narrow space of a racemic binding site. On the other hand, the absence of branching in a side chain in a group I chelate may increase the affinity toward a clay surface together with the effects due to the carbonyl group in an amino-acid. The carbonyl group is attracted toward the silicate surface due to the ion-dipole interaction with an excess negative charge in a montmorillonite layer. The exceptional behaviour of the TrpO chelate may be interpreted by the affinity of indole ring toward a clay surface due to hydrogen bonding.

The observed side-chain effects demonstrate that the clay modified by a chiral compound can resolve an adsorbed molecule by discriminating the details of the periphery of the molecule. Although $[Ni(phen)_3]^{2+}$ is not very representative in nature, its method of chirality recognition in the interlamellar region is probably not unique. Therefore, once a clay is modified by a proper chiral substance, a racemic metal chelate or an organic compound, which is complexed with a metal ion, may well be resolved in passing through a natural clay layer. Such an ability may make a clay a medium on which the molecular asymmetry was copied from one molecule to another. A search for the mode of modification to resolve amino-acids or glucose will help to understand the mechanism of the occurrence of chirality in biological systems.

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