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SEPARATION OF ISOMERS OF COBALT(III) COMPLEXES BY LIQUID CHROMATOGRAPHY ON A COLUMN PACKED WITH A CLAY-RUTHENIUM(II) COMPLEX ADDUCT

Key Words—Hectorite, Chromatography, Optical resolution.

We have recently initiated the method of chromatographic resolution on a clay modified with an optically active metal chelate (Yamagishi, 1985). The method was based on the finding that a racemic mixture of tris(1,10-phenanthroline)iron(II), $[Fe(phen)_3]^{2+}$, was adsorbed in excess of two times the cation exchange capacity (CEC) of a clay while the enantiomer of the same chelate was adsorbed within the CEC (Yamagishi, 1981). The results indicate that a racemic mixture of $[Fe(phen)_3]^{2+}$ is adsorbed as a racemic pair, while the enantiomer of the same chelate is adsorbed in molecular units. These facts suggest that the surface of a clay modified with an optically active chelate is able to recognize the chirality of a molecule.

The above finding led to a column packed with an adduct of a clay and optically active $[Ru(phen)_3]^{2+}$ being used for liquid column chromatography. As a result, the material has revealed high capability in resolving a number of organic and inorganic racemic compounds (Nakamura, 1988). When the adducts of other kinds of ion-exchangers such as ion-exchange resins are used for the same purpose, quite low resolution is attained (Yamagishi, 1987). In this respect, a clay provides a unique material for recognizing the chirality of a molecule.

It is, however, unclear how a resolved molecule interacts with an optically active chelate. In the present study, the isomer separation of a neutral complex, $[Co(acac)_2(aa)]$ (acac = acetylacetonato; aa = amino acidato), has been studied on a clay column modified with optically active $[Ru(phen)_3]^{2+}$. Twelve complexes were synthesized and their chromatographic behaviors were compared under the same conditions. If selectivity depends on the subtle variation in the structures of the molecules, the results may provide clues to understanding the resolution mechanisms.

$[Co(acac)_2(aa)]$ was synthesized according to the method of Laurie (1968). The crude product was purified by eluting on an alumina column. The final product was identified by the elemental analyses, NMR, IR, UV, and circular dichroism spectra. A cation exchange resin was used as purchased (Diaion SK #1, Mitsubishi Kasei Ind. Co., Japan).

To prepare a column, 1.5 g of spherically shaped synthetic hectorite was dispersed in ethanol (Nakamura, 1988). An amount of lambda-$[Ru(phen)_3]Cl_2$ equivalent to the CEC was added to it. After centrifuging the suspension, about 90% of the chelate was adsorbed by hectorite. The resultant clay-chelate adduct was packed into a stainless steel tube (50 mm × 4.0 mm (i.d.)) under pressure. An adduct of the same chelate with a cation exchange resin was prepared in the same way. In this case, about 50% of lambda-$[Ru(phen)_3]Cl_2$ was adsorbed by the resin. The adduct was packed into a glass tube (30 mm × 6.0 mm (i.d.)) as a slurry at atmospheric pressure.

Chromatographic separation was performed at room temperature using ethanol as a solvent. About 10^{-6} mole of Co(III) complex was mounted on the column and eluted with ethanol at the flow rate of 0.2–1.0 mL/min. The elution of a molecule was monitored by the absorbance change at 350 nm. No elution of the Ru(II) chelate was observed for a clay column. For the column of an ion-exchange resin, the Ru(II) chelate was eluted continuously. Therefore, the eluted fractions were analyzed after removing the Ru(II) chelate by passing through a new cation-exchange resin.

Table 1 summarizes the chromatographic results. The selectivity depends on the structure of the coordinated amino acid. For aa = glycinato and alaninato, the delta-isomer shows the higher affinity towards the column. For aa = valinato, both isomers have equal affinity. For aa = leucinato and asparaginato, the lambda-isomer shows the higher affinity. For the alaninato complexes, delta-$[Co(acac)_2$(L-alaninato)] is eluted faster than delta-$[Co(acac)_2$(D-alaninato)]. Thus the absolute configuration of the coordinated alaninato molecule has a definite effect on the retention volume. For the chelates of other kinds of amino acids, the absolute configuration of a coordinate amino acid shows little effect on the elution behaviors.

In order to clarify the role of a clay, the resolution of $[Co(acac)_2$(glycinato)] was attempted on a column packed with an ion-exchange adduct of a cation-exchange resin with lambda-$[Ru(phen)_3]Cl_2$. In this case, the eluted solution of $[Co(acac)_2$(glycinato)] has no optical activity. Thus the column is unable to separate the isomers of this chelate.

X-ray diffraction patterns were recorded for: (1) a powder sample of a clay-lambda-$[Ru(phen)_3]^{2+}$ adduct after being soaked in ethanol for one week, (2) a powder of the same adduct after being soaked in an ethanol solution with 1 mM of $[Co(acac)_2$(glycinato)] for one week, and (3) a powder of the same adduct after being

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Table 1. Effect of a co-ordinated amino acid (aa) on the steroselectivity of $[Co(acac)_2(aa)]$.

Amino acid (aa)	Side chain	Retention volume (V_1) ml	Retention volume (V_2) ml	Separation factor (α)[1]
D,L-glycine	-H	4.6 (Λ)	7.2 (Δ)	1.6
D,L-alanine	$-CH_3$	2.6 (Λ)	3.3 (Δ)	1.3
D-alanine		2.6 (Λ)	4.0 (Δ)	1.6
L-alanine		2.4 (Λ)	3.0 (Δ)	1.3
D,L-valine	$-CH(CH_3)_2$	1.3 (Δ)	1.3 (Λ)	1
D-valine		1.2	1.2	1
L-valine		1.2	1.2	1
D,L-leucine	$-CH_2CH(CH_3)_2$	1.1 (Δ)	1.1 (Λ)	1
D-leucine		1.0 (Δ)	1.2 (Λ)	1.2
L-leucine		1.1 (Δ)	1.2 (Λ)	1.2
L-asparagine	$-CH_2CONH_2$	2.8 (Δ)	3.6 (Λ)	1.3
Acetyl acetone	$OC(CH_3)CHCO(CH_3)^-$	0.56 (Δ)	0.86 (Λ)	2.4

[1] Separation factor is defined as

$\alpha = (V_2 - V_D)/(V_1 - V_D)$ $V_D = 0.34$ ml

in which V_D is the dead volume of the column.

soaked in an ethanol solution of 1 mM with $[Co(acac)_3]$ for one week. The basal spacings of these three samples are identical, 17.8 Å, within the experimental error. For samples (2) and (3), no measurable uptake of $[Co(acac)_2(glycinato)]$ or $[Co(acac)_3]$ by a clay is observed, respectively. The Ru(II) chelate is intercalated in the clay layers but the cobalt(III) chelates are not intercalated either for a clay or a clay-$[Ru(phen)_3]^{2+}$ adduct.

The binding energy, E, of $[Co(acac)_2(glycinato)]$ with the adduct of a clay and lambda-$[Ru(phen)_3]^{2+}$ was calculated by a procedure described in Sato *et al.* (1991). The intermediate complex between lambda-$[Ru(phen)_3]^{2+}$ and $[Co(acac)_2(glycinato)]$ was assumed to have formed on an external surface of the clay. Secondly, a bound $[Ru(phen)_3]^{2+}$ molecule was assumed to be adsorbed on a clay surface with its three-fold symmetry axis perpendicular to the surface (Taniguchi *et al.*, 1991). When $[Ru(phen)_3]^{2+}$ is adsorbed to 100% of CEC, one chelate occupies about 200 Å^2 per molecule. Thus there exists enough room for the adsorption of a Co(III) chelate between the pre-adsorbed $[Ru(phen)_3]^{2+}$ molecules.

Two kinds of stacking models were assumed: (A) the Co(III) chelate is located above the Ru(II) chelate and (B) the Co(III) chelate is located by the side of the Ru(II) chelate. For both models, the distance between the Co(III) atom and the Ru(II) atom is fixed at 8 Å. This length is chosen because the two complexes form a close association without steric interference at this distance. The rotation angle of the Co(III) chelate around the three-fold symmetry axis is chosen so that the binding energy is minimal.

The binding energies for two isomers for each stacking model are compared in Table 2. The lambda isomer of $[Co(acac)_2(glycinato)]$ has lower binding energy than the delta isomer for the A-stacking model. To the contrary, the delta isomer of $[Co(acac)_2(glycinato)]$ has lower binding energy than the lambda isomer for the B-stacking model. The intermediate of $Co(acac)_2(glycinato)]$ and $[Ru(phen)_3]^{2+}$ assumes the B-structure (side-by-side). This is because the delta isomer shows a higher affinity towards the column than the lambda isomer (Table 2). The calculation results do not explain why the intermediate does not take the A-structure even though it has more negative binding energy than the B-structure. One reason for this is that the calculation does not include the effect of solvent molecules.

For the present column, the separation of the isomers is accomplished by the intermolecular stacking interactions between the cobalt chelate and the pre-adsorbed lambda-$[Ru(phen)_3]^{2+}$. The present observation of the amino acid effects on the separation selectivity of $[Co(acac)_2(aa)]$ isomers (Table 1) gives us an example that the stability of a stacking intermediate is affected drastically by the structure of a ligand molecule. The model calculation of the interaction energy of $[Co(acac)_2(glycinato)]$ with a pre-adsorbed lambda-

Table 2. Calculated energy of $[Co(acac)_2(glycinato)]$ with an adduct of a clay and lambda-$[Ru(phen)_3]^{2+}$.

Configuration of co-chelate	Stacking mode[1]	Interaction energy with a clay (E_1) /kJ mole^{-1}	Interaction energy with Ru-chelate (E_2) /kJ mole^{-1}	Total energy ($E_1 + E_2$) /kJ mole^{-1}
Lambda-isomer	A	−70.5	−58.7	−129.2
Lambda-isomer	B	−139.0	+146.0	+7.0
Delta-isomer	A	−77.0	−32.8	−44.2
Delta-isomer	B	−145.7	+116.6	−29.1

[1] A = stacked, B = side-by-side. The distance between Co(III) and Ru(II) is taken to be 8 A.

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$[Ru(phen)_3]^{2+}$ on a clay supports that the interactions between these chelates take place in the stereoselective manners. The role of a silicate surface in the formation of such a stacking intermediate is certain to exist because an ion-exchange adduct of $[Ru(phen)_3]^{2+}$ and a cation exchange resin is unable to resolve $[Co(acac)_2(glycinato)]$.

Ru(II) chelates are adsorbed at higher density on a clay surface than on a cation-exchange resin. Moreover the chelates are oriented in the same direction on a clay surface. Thus a resolved molecule has a possibility to interact with more than one Ru(II) chelate simultaneously. Chirality recognition of an adsorbed molecule may be enhanced under such situations.

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