Chromium(III) Complexes with Amino Acids. II. Chromium(III) Complexes with L-α-Amino Acids

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As chromium(III) complexes with L-α-amino acids (alanine, aminobutyric acid, norvaline, norleucine, valine, isoleucine and leucine), $[Cr(ala)_3]$, (+)$[Cr(am\text{-}but)_3]$, $[Cr(OH)(am\text{-}but)_2]_2$, (+) and (−)$[Cr(norval)_3]$, (−)-$[Cr(norleu)_3]$, $[Cr(OH)(norleu)_2]_2$, $[Cr(val)_2(val\text{–}O)(NH_3)]$, (+)$[Cr(isoleu)_3]$, $[Cr(isoleu)_2(isoleu\text{–}O)(NH_3)]$, $[Cr(OH)(isoleu)_2]_2$, (+) and (−)$[Cr(leu)_3]$, and $[Cr(OH)(leu)_2]_2$ were prepared by the matrix method in solid state, and $[Cr(ala)_3]$, $[Cr(am\text{-}but)_3]$, $[Cr(OH)(am\text{-}but)_2]_2$, (−)$[Cr(norval)_3]$, $[Cr(OH)(norval)_2]_2$, (−)[Cr-$(norleu)_3]$, $[Cr(OH)(norleu)_2]_2$, (+)$[Cr(val)_3]$, $[Cr(val)_2(val\text{–}O)(NH_3)]$, $[Cr(OH)(val)_2]_2$, (+)$[Cr(isoleu)_3]$, $[Cr(OH)(isoleu)_2]_2$, and a mixture of diasteroisomers of $[Cr(leu)_3]$ were obtained by the usual method in solution. Some differences in the formation of the tris-type and hydroxo-dimer complexes appeared between the two methods. Especially, in the solid reaction, some complexes gave diastereoisomers with optically-active counter structures depending upon the kind of solvents used for preparation. All tris-type chromium(III) complexes with L-α-amino acids were of *fac*-structure.

In a previous paper,[1] systematic studies were reported on the effect of the length of the skeletal carbon chain or the presence of side chains in glycine and racemic amino acids upon the formation of complexes by the isothermal matrix method in solid state and by the usual method in solution in which hexaamminechromium(III) nitrate was used as the starting material. In the present work, attempts were made to prepare chromium(III) complexes with L-α-amino acids (alanine, aminobutyric acid, norvaline, norleucine, valine, isoleucine and leucine) by applying the same methods as described in Ref. 1 with respect to the preparation of racemic amino acids and to study the difference between racemic and L-amino acids in complexation. The studies of the formation of optical isomers of the complexes were also investigated.

Experimental

Preparation of Chromium(III) Complexes. There are two methods for the preparation of chromium(III) complexes with L-α-amino acids depending on the starting technique.

a) Preparation by Solid State Reaction: Hexaamminechromium(III) nitrate was mixed with the respective L-amino acid in a mortar. The mixture was heated at (150±1)°C in a Toyoroshi electronic drying oven. The molar ratio of the amino acids to the starting complexes was 3: 1 and the heating time was 20 min.

The reaction product containing L-alanine was dissolved in water. After removal of the residue by filtration, filtrate was kept standing at room temperature for one or two days. $[Cr(ala)_3]$ was gradually deposited as pink crystals. The main product of the residues was also $[Cr(ala)_3]$. Using a method similar to that described above, the di-μ-hydroxo-tetrakis-(amino acidato)dichromium(III) complexes were obtained as light purple crystals, when the amino acid was L-α-aminobutyric acid, L-norleucine or L-leucine. The complex with L-norvaline was, however, obtained as (−) $[Cr(norval)_3]\cdot 3H_2O$. In the case of L-isoleucine, a mixture of pink and purple crystals was gradually deposited. The mixture was dissolved in DMF. After filtration, the filtrate was added dropwise to water, causing instant precipitation of (+)$[Cr(isoleu)_3]\cdot 3H_2O$ as pink crystals. The purple residue obtained by the above filtration was $[Cr(OH)(isoleu)_2]_2\cdot 6H_2O$.

The reaction products containing L-α-aminobutyric acid, L-norvaline, L-norleucine, L-valine, L-isoleucine and L-leucine were dissolved in methanol. After removal of the residues by filtration, the filtrates were kept standing at room temperature for two or three days. (+)$[Cr(am\text{-}but)_3]\cdot H_2O$, (+)$[Cr(norval)_3]\cdot 2H_2O$, $[Cr(norleu)_3]\cdot 3H_2O$, $[Cr(val)_2(val\text{–}O)(NH_3)]\cdot 2H_2O$, $[Cr(isoleu)_2(iaoleu\text{–}O)(NH_3)]\cdot 2H_2O$ and (+)-$[Cr(leu)_3]\cdot 3.5H_2O$ were gradually deposited as pink crystals. After filtering the (+)$[Cr(am\text{-}but)_3]\cdot H_2O$ obtained above, the filtrate was kept standing at room temperature until completely dried, another type of $[Cr(am\text{-}but)_3]\cdot H_2O$ also being obtained as pink crystals. The former was soluble, whereas the latter was insoluble in water. The complexes $[Cr(val)_2(val\text{–}O)(NH_3)]\cdot 2H_2O$ and $[Cr(isoleu)_2(isoleu\text{–}O)(NH_3)]\cdot$ were obtained by drying for 30 min the above-mentioned crystals deposited at 50°C.

When ethanol was used as the solvent, tris type complexes were obtained as pink crystals only for L-norvaline, L-norleucine and L-leucine. The CD sign of these optically active tris type complexes was, however, negative, which is opposite to that of the corresponding complexes obtained in methanol. Complexes with L-valine and L-isoleucine were also obtained as $[Cr(val)_2(val\text{–}O)(NH_3)]\cdot 2H_2O$ and $[Cr(isoleu)_2(isoleu\text{–}O)(NH_3)]\cdot 2H_2O$, respectively, although they might have been contaminated by small amounts of tris type complexes. In the case of L-α-aminobutyric acid, only an oily substance was obtained, the crystallization having been unsuccessful. In the case of L-alanine, the reaction product was insoluble in both ethanol and methanol.

The analytical data for the complexes obtained by the above method are shown in Table 1, except for the dimer-complexes with isoleucine and norleucine. The IR spectra of these complexes were coincident with those of the corresponding complexes obtained by the solution method.

b) Preparation by Solution Reaction: Hexaamminechromium-(III) nitrate (345 mg) and L-α-alanine (267 mg) were dissolved in hot water (5 ml) and the mixture was heated in a water bath until pink crystals began to appear and then was cooled to room temperature. The pink crystals obtained were $[Cr(ala)_3]$. By applying the method described above, the complexes with L-α-aminobutyric acid, L-norvaline and L-valine were all precipitated as pink crystals. The pink crystals containing L-norvaline were dissolved in DMF or DMSO. After filtration, the filtrate was added dropwise to water, causing instant precipitation of (−)$[Cr(norval)_3]\cdot 3H_2O$. The pink complex containing L-α-aminobutyric acid was washed with water and then with ethanol. In the case of L-valine, the pink crystals were

Table 1. Analytical data (for the solid reaction)

Complexes	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
$[Cr(ala)_3]$[a]	34.18	34.12	5.74	5.75	13.29	14.11
$[Cr(am\text{-}but)_3]\cdot H_2O$[b]*	38.30	37.92	6.96	6.63	11.17	11.06
$[Cr(am\text{-}but)_3]\cdot H_2O$[b]**	38.30	38.40	6.96	6.55	11.17	11.18
$[Cr(norval)_3]\cdot 3H_2O$[a]	39.61	39.52	7.92	7.84	9.24	9.19
$[Cr(norval)_3]\cdot 2H_2O$[b]	41.28	40.71	7.39	7.14	9.63	9.76
$[Cr(norval)_3]\cdot 3H_2O$[c]	39.61	39.63	7.92	7.52	9.24	9.20
$[Cr(norleu)_3]\cdot 3H_2O$[b]	43.54	43.75	8.53	8.15	8.46	8.53
$[Cr(norleu)_3]\cdot 3H_2O$[c]	43.54	43.43	8.53	8.17	8.46	8.42
$[Cr(isoleu)_3]\cdot 3.5H_2O$[a]	42.77	42.51	8.57	8.07	8.31	8.53
$[Cr(leu)_3]\cdot 3.5H_2O$[b]	42.77	42.73	8.57	7.99	8.31	8.21
$[Cr(leu)_3]\cdot 2H_2O$[c]	45.18	44.90	8.43	8.60	8.78	9.16
$[Cr(val)_2(val\text{-}O)(NH_3)]\cdot 2H_2O$[b]	40.00	39.49	7.61	7.75	12.43	12.25
$[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]\cdot 2H_2O$[b]	43.62	44.06	8.74	8.18	11.31	11.19
$[Cr(OH)(am\text{-}but)_2]_2\cdot 1.5H_2O$[a]	33.51	33.79	6.45	5.88	9.77	9.90
$[Cr(OH)(leu)_2]_2\cdot 6H_2O$[a]	37.59	36.53	8.65	7.96	7.71	7.31

Solvent: a) water, b) methanol, c) ethanol. * dissolved in water, ** not dissolved in water.

Table 2. Analytical data (for the solution reaction)

Complexes	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
$[Cr(ala)_3]$	34.18	33.18	5.74	5.49	13.29	13.17
$[Cr(am\text{-}but)_3]\cdot H_2O$	38.30	38.12	6.96	6.60	11.17	11.10
$[Cr(norval)_3]\cdot 3H_2O$	39.61	40.16	7.92	7.10	9.24	9.35
$[Cr(norval)_3]\cdot 3H_2O$	39.61	39.75	7.92	7.10	9.24	9.09
$[Cr(norleu)_3]\cdot H_2O$	46.95	46.44	8.32	8.27	9.12	8.87
$[Cr(val)_3]\cdot 3H_2O$	39.61	39.60	7.92	7.75	9.24	9.25
$[Cr(isoleu)_3]\cdot 3H_2O$	43.54	43.41	8.53	8.33	8.46	8.41
$[Cr(leu)_3]\cdot 2H_2O$	45.18	46.05	8.43	8.40	8.78	8.93
$[Cr(OH)(am\text{-}but)_2]_2\cdot 1.5H_2O$	33.51	33.44	6.45	6.13	9.77	10.30
$[Cr(OH)(norval)_2]_2\cdot 2H_2O$	37.62	37.39	7.26	7.01	8.77	8.53
$[Cr(OH)(norleu)_2]_2\cdot 4H_2O$	39.45	40.06	8.00	7.67	7.67	7.88
$[Cr(OH)(val)_2]_2\cdot 2H_2O$	37.62	36.91	7.26	6.52	8.77	8.78
$[Cr(OH)(isoleu)_2]_2\cdot 6H_2O$	37.59	37.04	8.65	8.15	7.31	7.32

dissolvaed in ethanol. After filtration, $(+)[Cr(val)_3]\cdot 3H_2O$ was obtained from the residue and when the filtrate was allowed to stand at room temperature for three or four days, $[Cr(val)_2(val\text{-}O)(NH_3)]\cdot xH_2O$ was gradually deposited as red-purple crystals. By heating at 50°C for 30 min, the amount of crystal water contained was determined to be $x=2$. The IR spectrum of this complex was coincident with that of the corresponding complexes obtained for the solid state reaction.

By using a similar method, with the exception that 60 ml of water was employed insteaed of 5 ml of hot water, hydroxo-dimer complexes with L-α-aminobutyric acid, L-norvaline, L-norleucine, L-valine and L-isoleucine were obtained as purple crystals. However, the complexes with L-alanine and L-leucine were of tris-type. When 10 ml of water was employed, hydroxo-dimer complexes were obtained in the case of L-α-aminobutyric acid and L-valine, whereas only tris complexes were obtained for all the other amino acids. The tris complex containing L-norvaline was dissolved in methanol. After filtration, the filtrate was concentrated using a cooling dryer, causing the precipitation of $(-)[Cr(norval)_3]\cdot 3H_2O$. The residue thus obtained was identical to that obtained previously.

The analytical data of these complexes are shown in Table 2.

Apparatus. The UV spectra were measured with a Hitachi 139 spectrophtometer. The IR spectra were measured in a KBr disk with a Hitachi EPI-G3 infrared spectrophtometer. The CD spectra were recoded on a JASCO Model ORD/UV-5 spectrophtometer with a CD attachment.

Results and Discussion

UV Absorption Spectra. The absorption spectra of the chromium(III) complexes with L-α-amino acids of type $[Cr(L)_3]$ and $[Cr(L)_2(L\text{–}O)(NH_3)]$, where L denotes amino acids, were measured in DMSO, except for the complexes with alanine, aminobutyric acid and norleucine which were insoluble in DMSO. The spectra of the chromium(III) complexes with alanine and aminobutyric acid were measured in solid state and in perchloric acid. The spectrum of the tris(norleucinato)-chromium(III) complex was not measured, because the yield of this complexes was very small. Since the color of this complex was pink, the structure may be of facial form.

The numerical data for their absorption maxima are summarized in Table 3. These data suggest that the

Table 3. Absorption maxima of tris- and bis-type chromium(III) complexes

ν: wave number of absorption maximum,
ε: molar absorption coefficient (M^{-1} cm^{-1} M: mol dm^{-3}).

	$\nu_1/10^3$ cm^{-1}	(log ε)	$\nu_2/10^3$ cm^{-1}	(log ε)	Solvent
Solid state reaction					
$[Cr(ala)_3]$	18.7	(1.71)	25.1	(1.62)	20%$HClO_4$
$[Cr(ala)_3]$	19.4		26.0		Reflectance
$[Cr(am\text{-}but)_3]$	19.4	(1.87)	26.0	(1.83)	DMSO
$[Cr(am\text{-}but)_3]$	18.6	(1.70)	25.0	(1.64)	20%$HClO_4$
$[Cr(norval)_3]$[a]	19.5	(2.20)	25.7	(2.09)	DMSO
$[Cr(norval)_3]$[b]	19.2	(2.24)	25.3	(2.11)	DMSO
$[Cr(norval)_3]$[c]	19.5	(2.22)	25.7	(2.10)	DMSO
$[Cr(norleu)_3]$	19.5	(2.25)	25.7	(2.05)	DMSO
$[Cr(isoleu)_3]$	19.2	(2.24)	25.3	(2.14)	DMSO
$[Cr(leu)_3]$[b]	19.2	(2.30)	25.3	(2.20)	DMSO
$[Cr(leu)_3]$[c]	19.4	(2.29)	25.5	(2.20)	DMSO
$[Cr(val)_2(val\text{-}O)(NH_3)]$	19.3	(1.76)	25.7	(1.81)	DMSO
$[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$	19.3	(1.75)	25.7	(1.82)	DMSO
Solution state reaction					
$[Cr(ala)_3]$	19.4		26.0		Reflectance
$[Cr(am\text{-}but)_3]$	18.6	(1.70)	25.0	(1.65)	20%$HClO_4$
$[Cr(am\text{-}but)_3]$	19.4		26.0		Reflectance
$[Cr(norval)_3]$	19.5	(2.19)	25.7	(2.08)	DMSO
$[Cr(norleu)_3]$	19.5	(2.27)	25.7	(2.06)	DMSO
$[Cr(val)_3]$	19.1	(2.24)	25.4	(2.08)	DMSO
$[Cr(isoleu)_3]$	19.2	(2.24)	25.4	(2.12)	DMSO
$[Cr(leu)_3]$	19.3	(2.28)	25.4	(2.20)	DMSO

Solvent: a) water, b) methanol, c) ethanol.

complexes with L-alanine and L-α-aminobutyric acid undergo acid hydrolysis or some chemical reaction on dissolution in perchloric acid and that the behavior is similar to that of complexes with *dl*-alanine and *dl*-α-aminobutyric acid. Also it is seen that the absorpiton maxima of the other chromium(III) complexes are almost coincident with those of the corresponding chromium(III) complexes of tris-type with *dl*-amino acids.[1] This suggests that the chromium(III) complexes

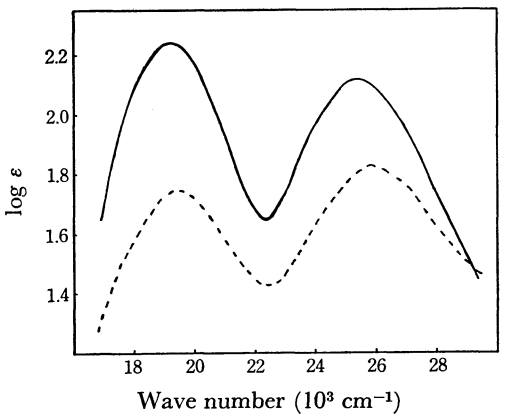

Fig. 1. The absorption spectra of $[Cr(isoleu)_3]$ (——) and $[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$ (------) in DMSO solution.
ε: M^{-1} cm^{-1}, M: mol dm^{-3}.

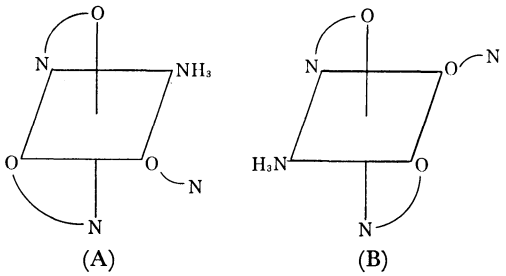

Fig. 2. The possible structures of $[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$.

of tris-type are of *fac*-structure.

The spectra of $[Cr(isoleu)_3]$ and $[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$ in DMSO are shown in Fig. 1. The absorption curve of the bis-type complex is similar to that of the tris-type, except that the first absorption band has a lower absorption coefficient than the second band of the bis-type complex. Therefore, this uggests that the coordinating structure of the bis-type complex is a cis-cis structure with respect to the nitrogen or oxygen atoms and the symmetry of this complex is lower than the C_{3v} of tris-type complex. Thus, for the bis-type complex, two geometrically possible isomers are considered, as shown in Fig. 2. When the reaction product was dissolved in water, instead of methanol, a mixture of *fac*- and hydroxo-dimer complexes were obtained. This suggests that the coordinating structure of this complex is that of (A) in Fig. 2. The absorption spectrum of $[Cr(val)_2(val\text{-}O)(NH_3)]$ was similar to that of $[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$. The structure of the bis(valinato) complex is also coincident with that of the bis(isoleucinato) one.

IR Spectra. Infrared absorption spectra were measured in the range of 4000 to 400 cm^{-1}. The spectra of $[Cr(isoleu)_3]$ and $[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$ are shown in Fig. 3. It is seen from this firgure that the absorption peak which is assigned to the NH_2 deformation vibration appears at 1505 cm^{-1} in the bis-type complex, but that in the tris complex in which all amine groups were bonded to the chromium atom, this peak is shifted to 1600 cm^{-1}. Therefore, these results lead to the conclusion that the structure of this bis-type complex is that of (A) in Fig. 2. The bis-type

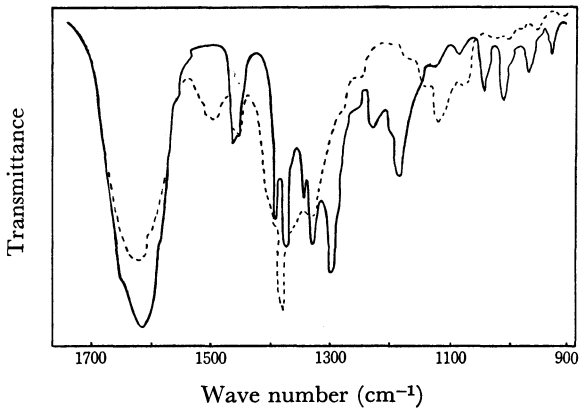

Fig. 3. The IR spectra of $[Cr(isoleu)_3]$ (——) and $[Cr(isoleu)_2(isoleu\text{-}O)(NH_3)]$ (------).

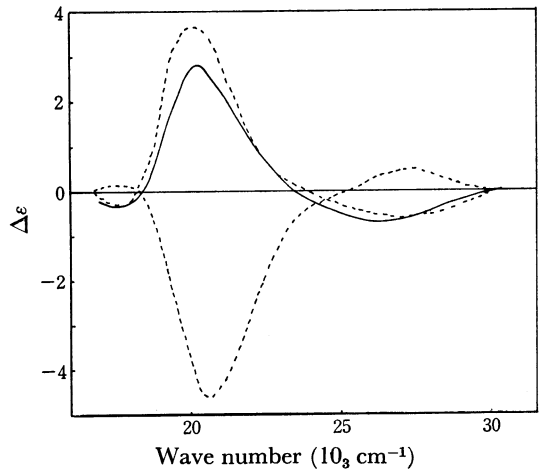

Fig. 4. The CD spectra of (+)[Cr(L-am-but)$_3$] (——) and (+) and (−)[Cr(L-norval)$_3$] (------).
ε: M^{-1} cm^{-1}, M: mol dm^{-3}.

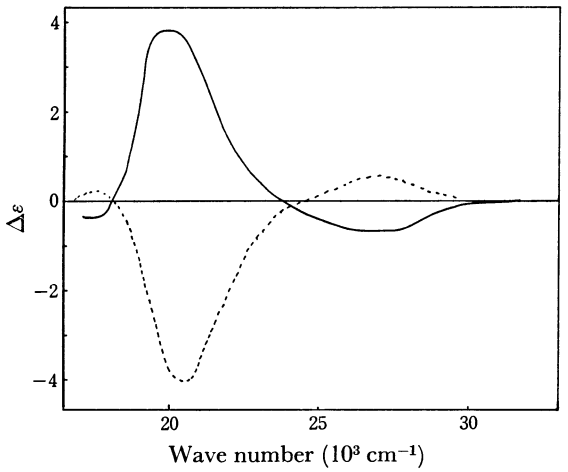

Fig. 5. The CD spectra of (−)[Cr(L-norleu)$_3$] (------) and (+)[Cr(L-val)$_3$]] (——).
ε: M^{-1} cm^{-1}, M: mol dm^{-3}.

complex with L-valine also has an absorption peak at 1505 cm^{-1}. This suggests that the structure of this complex is similar to that of the bis-type complex with L-isoleucine.

CD Spectra. The circular dichroism for (+)[Cr(am-but)$_3$] and (+) and (−)[Cr(norval)$_3$] (Fig. 4), (−)[Cr(norleu)$_3$] and (+)[Cr(val)$_3$] (Fig. 5), and (+)[Cr(isoleu)$_3$] and (+) and (−)[Cr(leu)$_3$] (Fig. 6) were measured in DMSO. Although the separation of these optical isomers was not always perfect, the $\Delta\varepsilon_{(ext)}$ of the major components of the first absorption band were larger than those for the corresponding cobalt(III) complexes.[2] Therfore, it appears that these optical isomers were obtained as complexes with fairly high optical purity. Their configurations can be tentatively identified as *Λ* for (+) and *Δ* for (−) by comparing the CD curves of the present complexes with those of the *Λ*-tris(oxalato)[3] and *Λ*-tris(ethylendiamine)chromium[4] ions, respectively. Gillard *et al.* have reported that [Cr(ala)$_3$] which is insoluble in water is of *Λ*-form.[5] The IR spectrum of [Cr(ala)$_3$] obtained in the present work agrees with that published by the above authors.

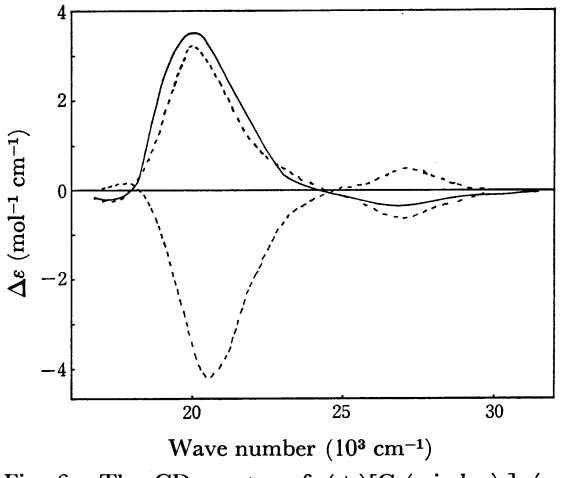

Fig. 6. The CD spectra of (+)[Cr(L-isoleu)$_3$] (——) and (+) and (−)[Cr(L-leu)$_3$] (------).
ε: M^{-1} cm^{-1}, M: mol dm^{-3}.

Douglas and Yamada have reported[6] that the lower solubility of (β)-*Λ*[Co(L-ala)$_3$] is not surprising since the molecules of the isomer might be expected to interact strongly through intramolecular hydrogen bonding which would be possible if the molecules were stacked directly above one another. The solubility of (+)[Cr(norval)$_3$] is appreciably lower than that of the corresponding (−) complex. Therefore, the tris(aminobutyrato) and tris(norleucinato)chromium(III) complexes, which are insoluble in both water and DMSO might be also of (+)-form. But, (+)[Cr(am-but)$_3$] which is soluble in water might be different from the other complexes in crystal structure. In general, the solubility of *fac*-(+)chromium(III) complexes with L-amino acids which do not have the side chain is lower than that of the (−) complexes. On the other hand, it is not difficult to understand that the solubility of (+)[Cr(val)$_3$], (+)[Cr(isoleu)$_3$] and (+)[Cr(leu)$_3$] is high, since the interaction through intramolecular hydrogen bonding would become weaker as these amino acids have a methyl group in the β- or γ-position. Since the spectra of [Cr(val)$_2$(val–O)(NH$_3$)] and [Cr(isoleu)$_2$-(isoleu–O)(NH$_3$)] were not observed, except for the small peaks which are regarded as due to vicinal effects, these complexes are considered to be mixturees of diastereoisomers.

Table 4. Chromium(III) complexes prepared with L-amino acids

Amino acid	[Cr(L)$_3$]	[Cr(L)$_2$-(L–O)(NH$_3$)]	[Cr(OH)-(L)$_2$]$_2$
Alanine	◑		
Aminobutyric acid	◑		◑
Norvaline	◑		○
Norleucine	◑		◑
Valine	○	◑	○
Isoleucine	◑	●	◑
Leucine	◑		●

L=amino acid.
●: Complexes prepared by the solid method.
◑: Complexes prepared by both methods.
○: Complexes prepared by the solution method.

The chromium(III) complexes with various L-α-amino acids of type $[Cr(L)_3]$, $[Cr(L)_2(L\text{–}O)(NH_3)]$ and $[Cr(OH)(L)_2]_2$ were synthesized in solid state and in solution (Table 4). The preparation of chromium(III) complexes with natural L-α-amino acids by the two methods may be characterized as follows.

i) *Solid State Reaction.* The complexes of tris-type structure were prepared for all amino acids, except for L-valine, but the complexes of dimer-structure were prepared only for amino acids other than L-alanine, L-norvaline and L-valine. As far as valine and isoleucine, which have a methyl group in the β-position, are concerned, a new type complex, $[Cr(L)_2(L\text{–}O)(NH_3)]$ was prepared. When water was used as the solvent, the complexes containing alanine and norvaline obtained were of tris-type, while the complexes containing aminobutyric acids and norleucine were of dimer structure. Complexes with L-α-amino acids are predominatly of tris- and dimer-type, alternatively, depending on the length of the carbon skeleton. This is also observed for the complexes with racemic amino acids prepared by the solution method.

Table 5. Optical isomers of the tris-chromium(III) complexes prepared

Amino acid	Solid reaction			Solution reaction
	MeOH	EtOH	H_2O	
Alanine	no	no	(+)	(+)
Aminobutyric acid	+	no	no	(+)
Norvaline	+	−	−	−
Norleucine	(+)	−	−	−
Valine	no	no	no	+
Isoleucine	no	no	+	+
Leucine	+	−	no	mixture

no: No tris-complex was obtained.
( ): The CD spectrum was not measured due to the low solubility.

The interesting relation between the formation of optical isomers and the solvent in which the reaction product was dissolved, which is shown in Table 5, together with that for complexes prepared by the solution method. These data suggest that the preponderance of the type of optical isomers is changed depending upon the kind of solvent used, specifically, when reaction products were dissolved in methanol, (+) isomers were obtained, while (−) isomer were obtained in ethanol. The reason may be due to the difference in the solubilities of the diastereoisomers, although this is still not clear from the present work. When water was used as the solvent, the complex with alanine was obtained as a (+) isomer, but those with norvaline and norleucine in which the length of carbon chain is longer than that of aminobutyric acid are obtained as (−) isomers. On the other hand, the complexes with L-amino acids which have a side chain have no clear tendency, since the complex with L-isoleucine are obtained as a (+) isomer, while the other complexes obtained are not in tris form.

When the differences between the racemic and L-amino acids in the complexation were compared, L-amino acids which have no side chains were similar to the racemic acid, except for norleucine. The complexes with L-amino acids which have a side chain were obtained as bis- (val), tris-, bis- and dimer-(isoleu), and tris- and dimer-structures (leu), while the complexes with the corresponding racemic amino acids were obtained only as dimer-type structures. No circular dichroism for tris-type structures with racemic amino acids was observed, while the complexes with L-amino acids were found to be optically active.

ii) *Solution State Reaction.* The chromium(III) complexes with L-amino acids were all prepared as tris-type structures. All complexes of dimer-structure were prepared, except for alanine and leucine. By changing the amount of water in which the mixture was dissolved, tris- or dimer-complexes were selectively obtained. The optical isomer obtained by the solution method is similar to that resulting from the solid reaction which was dissolved in water, except for L-α-aminobutyric acid, L-valine and L-leucine which were not prepared as tris-type complexes in solid state.

When the differences between racemic and L-amino acids in complexation were compared, no significant difference was observed for the solution method, except that the complexes with L-amino acids were obtained as optically-active complexes. However, a different result was obtained for the complex with valine, since *dl*-valine gave only a dimer-type complex, while L-valine gave tris-, bis- and dimer-structures.

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