主論文

Metal Isotope Effects
on
the Vibrational Spectra
of
Polymeric Metallo-aminoacid Complexes

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Junichi Odō

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Preface

Recently, the importance of metal ions to the vital functions of living organisms has become increasingly apparent. It is very significant to investigate the coordination surrounding, stereochemistry and biological activity for metallo-aminoacids, -proteins and -enzymes which contain metal ions in order to investigate the roles of metal ions *in vivo* on the molecular level. On the other hand, the role of vibrational spectroscopy is increasing for investigating surface-conformations of the complicated vital molecules in relation to their catalytic site. However, while metallo-aminoacids have already received considerable attention by means of X-ray analysis and UV and visible, ESR, NMR and CD spectra, the vibrational spectra of metallo-aminoacids have rarely been investigated in detail. Probably, it is rather difficult to analyze the vibrational spectra of metallo-aminoacids by simple comparison with those of related complexes and aminoacids, since they frequently take a complicated polymeric structure. This may be one of the reasons why the vibrational spectra have been investigated in less detail than the crystallographic data and the other spectroscopic data. The author gave his attention to the metal isotope technique, which is very useful to assign the vibrations containing displacement of the metal unambiguously. In the present thesis, the vibrational spectra of metallo-aminoacids, on which much interest has been centered in their biological activities, are dealt with to obtain fundamental and definite informations concerning the vibrational spectroscopy for further investigations of metallo-proteins and -enzymes.

Chapters I - III deal with the infrared spectra of polymeric metallo-aminoacid complexes, bis(L-asparaginato)-copper(II) and -zinc(II) and copper(II)- and zinc(II)-L-glutamate dihydrates. It has been revealed that the metal isotope technique is very useful for assigning the metal-ligand stretching vibrations of the polymeric metal complexes. The difference of the metal-ligand stretching vibrations between the copper and zinc complexes is discussed.

Chapter IV deals with the infrared spectra of *trans*- and *cis*-bis(D-alaninato)copper(II) to aim at clarifying how the Cu-ligand stretching vibrations are affected by the *trans-cis* isomerism. The spectral difference between the *trans* and the *cis* isomers was investigated by the normal coordinate analyses by using a complete molecular conformation and the inter- and intramolecular force fields. Additionally, on the basis of the results of chapter IV, the relationship between infrared spectrum and *trans-cis* isomerism is discussed for bis(L- and DL-phenylalaninato)copper(II) in chapter V.

Chapter VI deals with the infrared spectra of bis(L-serinato)-copper(II) and -zinc(II) in order to clarify the difference of the vibrational spectra between *gauche-gauche* and *anti-gauche* serinates in the complexes. The structural difference is reflected clearly in the skeletal stretching and the COO deformation frequencies but not in the Cu-ligand stretching frequencies.

Chapter I

Infrared Spectra of Bis(L-asparaginato)copper(II)

I-1 Introduction

Much interest has been centered on polymeric metal complexes in relation to their roles in cancer chemotherapy and their biological activity.$^{1)}$ Among them, complexes including aminoacids and related compounds may be of interest in relation to the role of metals *in vivo* and have already received considerable attention from many investigators.$^{2-5)}$ However, in contrast with monomeric metal complexes of aminoacids, their vibrational spectra have rarely been investigated in detail because of their complicated structures. In this chapter, [bis(L-asparaginato)-copper(II)]$_n$, [Cu(asn)$_2$]$_n$, was studied as a model of polymeric metal complexes including aminoacids. Metal-ligand stretching frequencies of [Cu(asn)$_2$]$_n$ were assigned by using the metal isotope technique which has been shown to be effective for identifying vibrations involving the displacement of a metal atom.$^{6,7)}$ In addition to this technique, the frequency shifts of *N*,*N'*-deuteration were useful for making assignments.

I-2 Experimental

I-2.1 Materials

Commercially available L-asparagine monohydrate (asn·H_2O, Wako Junyaku) was purified several times by crystallization from water. Deuterated L-asparagine monohydrate (asn-d_5·D_2O) was obtained from the purified asn·H_2O by exchange reaction with heavy water (Merck, AG., 99%). $[Cu(asn)_2]_n$ was prepared from the purified asn·H_2O according to the method of Stephens *et al.*[8] For the preparation of *N,N'*-deuterated complexes, anhydrous cupric acetate was reacted with asn-d_5·D_2O in heavy water. The precipitate was filtered, washed with heavy water and dried under reduced pressure. For the preparation of complexes containing metal isotopes, ^{63}CuO and ^{65}CuO (Oak Ridge National Lab., USA) were converted into the corresponding cupric acetates by reaction with dilute acetic acid on a milligram scale. The cupric acetates were reacted with the asn·H_2O in water and the resulting solids were washed with water and dried under reduced pressure. The yield was about 40 mg of both complexes. The chemical purity of each complex containing isotopes was checked by comparing its IR spectrum with that of the complex containing metal of natural abundance. The isotopic purities were 99.89 % for ^{63}CuO and 99.70 % for ^{65}CuO.

I-2.2 Measurements

The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000 - 200 cm^{-1}). The measurements were made with solid samples in Nujol, hexachlorobutadiene and poly(chlorotrifluoroethylene) oil (Merck, AG., Uvasol) mulls. The frequencies were calibrated by means of the standard absorptions of polystyrene, indene and water vapor. For measuring small shifts of band centers due to ^{63}Cu and ^{65}Cu substitution, the scale of the frequency was expanded ten times over the desired frequency region, and the measurements were repeated three times to check the reproducibility of the spectra.

The IR spectra in the region above 400 cm^{-1} of asn·H_2O, $[Cu(asn)_2]_n$ and their deuterated analogues are shown in Fig. 1, and parts of the expanded spectra are shown in Fig. 2.

I-3 Assignments and Discussion

The region above 530 cm^{-1}.

According to neutron diffraction analysis,[9] asparagine takes a zwitterion structure in the monohydrate crystal. In this structure, the group vibrations of aminoacids and primary amides can be expected to resemble those of asparagine. By referring to the frequency shifts on deuteration and the IR spectra of related compounds, for example alanine,[10] glycine[11] and acetamide,[12,13] these group vibrations were tentatively

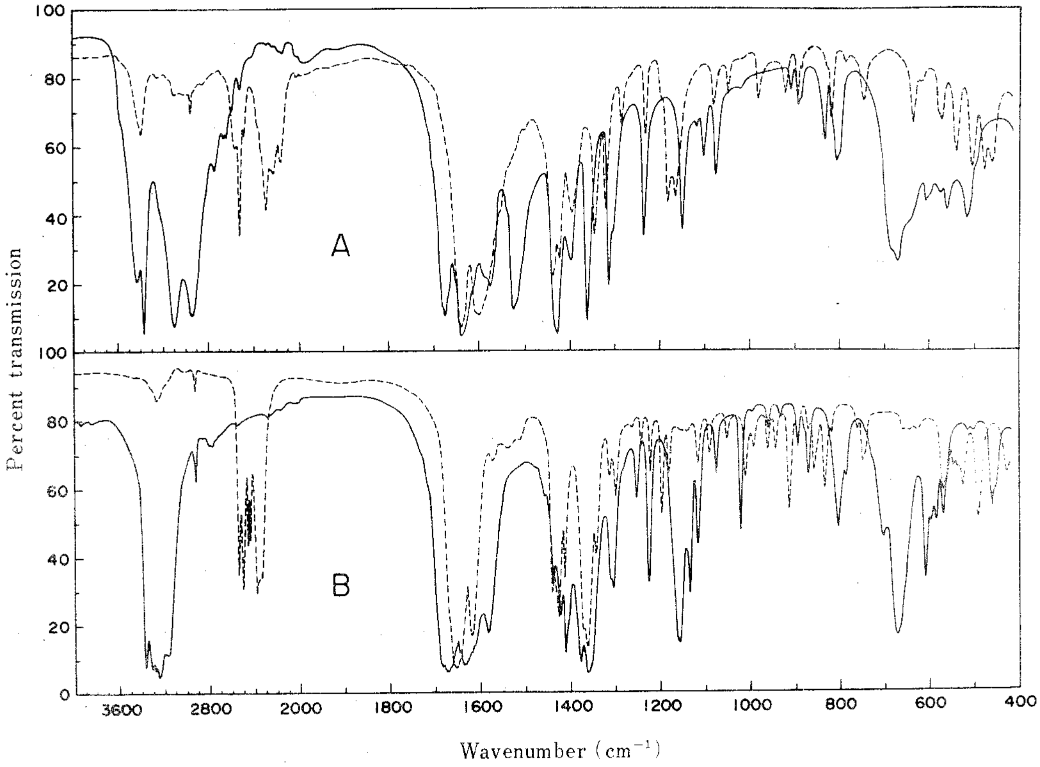

Fig. 1. IR Spectra of Asn·H_2O and $[Cu(asn)_2]_n$ in the Region above 400 cm^{-1}

A: asn·H_2O (——) and asn-d_5·D_2O (----); B: $[^{NA}Cu(asn)_2]_n$ (——) and $[^{NA}Cu(asn\text{-}d_4)_2]_n$ (----).

assigned as summarized in Table I.

Upon complex formation, the $-NH_3^+$ group of asn·H_2O is replaced by the $-NH_2$ group.[8,9] Except for the spectral change caused by this replacement, the IR spectrum in this region of $[Cu(asn)_2]_n$ is expected to be similar to that of asn·H_2O, and the ligand absorptions can be assigned to individual vibrations as shown in Table I by referring to the frequency shifts on *N*,*N'*-deuteration and the assignments of asn·H_2O and monomeric aminoacid complexes.[14-16] However, there are some noteworthy spectral changes upon complex formation. One of them is the spectral difference between asn·H_2O and $[Cu(asn)_2]_n$ in the region between 3500 and 2800 cm^{-1}. A band at 1520 cm^{-1} of asn·H_2O, assigned to the $-NH_3^+$ symmetrical deformation vibration, vanishes upon complex formation. Two bands of asn-d_5·D_2O assigned to the COO^- stretching vibrations undergo a high frequency shift by about 10-20 cm^{-1} upon complex formation in spite of the fact that the COO^- group coordinates to the Cu atom. The corresponding shift for the undeuterated compounds is not obvious because of the interference of the NH_2 and NH_3^+ group and water vibrations.

In the region above 530 cm^{-1}, no band shows appreciable shifts on ^{63}Cu and ^{65}Cu substitution. This result indicates that none of the vibrations in this region involve displacements of the Cu atom.

The region between 530 and 200 cm^{-1}.

By analogy with the IR spectra of aminoacid complexes,[14-16] the Cu-ligand stretching vibrations can be expected in this region. Strictly speaking, all the copper-ligand stretching vibrations of $[Cu(asn)_2]_n$ should be infrared-active because the Cu atom is in a tetragonally distorted octahedral environment and occupies a C_1 site.[9] However, since the carboxyl oxygen and the α-amino nitrogen atoms of each ligand coordinate to the copper atom in a *trans* square planar configuration and the two Cu-O' bonds are almost colinear with the normal to the coordina-

TABLE I. Infrared Frequencies and Assignments for Asn·H_2O and $[Cu(asn)_2]_n$ in the Region above 530 cm^{-1}

asn·H_2O	asn-d_5·D_2O	$[Cu(asn)_2]_n$	$[Cu(asn\text{-}d_4)_2]_n$	Assignments[c]
3443 s	2175 m	3375 vs	2549 s	νNH_2 (ND_2) or νNH_3^+ (ND_3^+) or νH_2O (D_2O)
3377 vs	2237 m	3319 vs	2515 s	
3103 vs	2302 s	3285 vs	2409 m	
2951 vs	2493 m	3255 vs	2447 s	
	2535 s	3175 vs	2387 s	
	2570 m		2349 s	
	2956 w	2925 w	2924 w	νCH_2 or νCH
1680 vs	1643 vs	1678 vs	1655 vs	$\nu C{=}O$
1643 vs	1605 vs	1640 vs	1624 s	$\nu_a COO^-$
—[a]	1184 m	1586 s	1199 m, 1183 w	βNH_2 (ND_2)
1580 s	1169 m	—[b]	—[b]	$\delta_d NH_3^+$ (ND_3^+)
1527 s	1082 w	—[b]	—[b]	$\delta_s NH_3^+$ (ND_3^+)
1430 vs	1442 s	1418 s	1426 m	νCN
	1428 s	1443 m, 1426 s	1443 m, 1430 m	δCH_2
1401 m	1400 m	1380 s, 1365 vs	1375 sh, 1366 vs	$\nu_s COO^-$
1363 s	1351 s	—[a]	1346 m	δCH
1316 s	1326 m	1321 sh, 1306 m	1318 w, 1302 m	ωCH_2
1306 sh	1290 w	—[a]	1265 vw	$t CH_2$
1236 m	1235 w	1254 w, 1226 m	1245 w, 1224 m	νskel
1151 m	925 w	1158 s	914 m	ρNH_2 (ND_2)
1104 m	749 m	—[b]	—[b]	ρNH_3^+ (ND_3^+)
—[b]	—[b]	1135 m	835 m, 750 m	$t NH_2$ (ND_2)
1075 m	1051 w	1119 m, 1077 w	1118 w, 1053 w	νskel
911 w	984 w	961 w, 935 w	962 w, 945 w	νskel
894 w	898 w	896 w	896 w	νskel
834 m	822 m	872 m	859 m	ρCH_2
808 m	480 m	804 m	525 m	τNH_2 (ND_2)
685 sh	461 m	669 s	490 m	ωNH_2 (ND_2)
670 vs	639 m	702 w	646 vw	δskel
—[b]	—[b]	606 s	430 m	ωNH_2 (ND_2)
604 m	574 w	594 sh	568 m	δskel
573 m		582 m	561 sh	δskel
558 m	542 m	567 m	545 vw, 535 sh	δskel

a) Hidden by a neighboring band.
b) Not expected.
c) ν: stretching; β: bending; δ: deformation; ω: wagging; ρ: rocking; t: twisting; τ: torsion.

tion square plane,$^{9)}$ it is a reasonable approximation to classify the Cu-ligand stretching vibrations into symmetrical and asymmetrical modes for the Cu atom. The latter can be expected to be relatively strong in the IR spectrum and to be sensitive to ^{63}Cu and ^{65}Cu substitution, in contrast with the symmetrical modes.

$[Cu(asn)_2]_n$ shows strong bands at 459, 450, 391, 360, 318 and 212 cm^{-1} in this region. On simple comparison with the IR spectra of asn·H_2O and $[Cu(asn)_2]_n$, the 391, 360 and 318 cm^{-1} bands seem to correspond to the ligand bands at 390, 352 and 296 cm^{-1}, respectively. The 459 and 450 cm^{-1} bands seem to appear newly upon complex formation and might be due to the Cu-ligand stretching vibrations. In contrast with expectation, these bands remain almost unshifted on ^{63}Cu and ^{65}Cu substitution, but are replaced by two bands at 411 and 427 cm^{-1} on *N,N'*-deuteration. This result strongly indicates that the 459 and 450 cm^{-1} bands require displacement not of the Cu atom, but of the nitrogen atoms. Thus, these bands should be assigned to skeletal deformation vibrations of the ligands. The frequency difference of these vibrations between asn·H_2O and $[Cu(asn)_2]_n$ may be caused by coupling with the Cu-N stretching vibration and/or the structure change of asparagine upon complex formation. The 318 and 360 cm^{-1} bands show 2.1 and 1.5 cm^{-1} shifts, respectively, on ^{63}Cu and ^{65}Cu substitution, and are assigned to vibrations involving displacement of the Cu atom. On *N,N'*-deuteration, the 318 cm^{-1} band shows a relatively small isotope shift, but the 360 cm^{-1} band is replaced by a band at 327 cm^{-1}. Accordingly, the former was assigned to the Cu-O asymmetrical stretching vibration and the latter to the Cu-NH$_2$ asymmetrical stretching vibration. The 391 and 212 cm^{-1} bands are unaffected by ^{63}Cu and ^{65}Cu substitution, but are replaced by bands at 369 and below 200 cm^{-1} on *N,N'*-deuteration, respectively, and were assigned to skeletal deformation vibrations of the ligands.

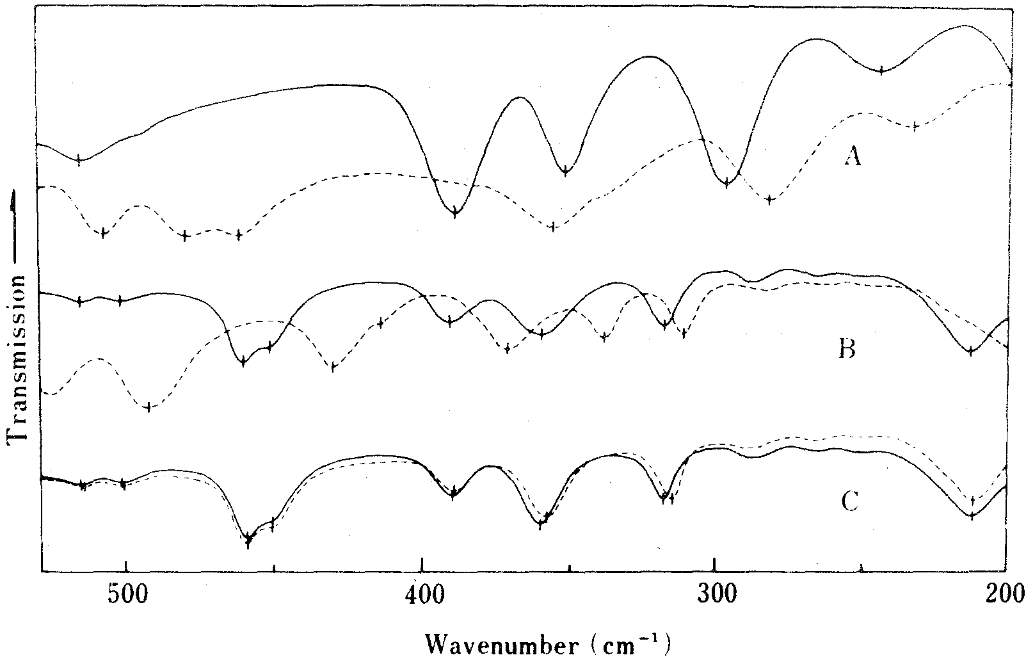

Fig. 2. IR Spectra of Asn·H$_2$O and [Cu(asn)$_2$]$_n$ in the Region between 530 and 200 cm^{-1}

A: asn·H$_2$O (——) and asn-d_5·D$_2$O (----); B: [^{NA}Cu(asn)$_2$]$_n$ (——) and [^{NA}Cu(asn-d_4)$_2$]$_n$ (----); C: [^{63}Cu(asn)$_2$]$_n$ (——) and [^{65}Cu(asn)$_2$]$_n$ (----).

TABLE II. Infrared Frequencies, Isotope Shifts and Assignments in the Region below 530 cm^{-1}

asn·H_2O	asn-d_5·D_2O	$[^{63}Cu(asn)_2]_n$	$\Delta\nu_m$[b)]	$\Delta\nu_h$[c)]	Assignments[d)]
515 m	*a*)				δskel
		514.3 vw	0.7	*e*)	δskel or ν_sCu-ligand
		499.7 vw	0.2	*e*)	δskel or ν_sCu-ligand
390 m	350 m	458.9 m	0.1	31	δskel
352 m	337 sh	450 sh	~0	39	δskel
296 m	282 m	390.6 w	0.2	22	δskel
		359.6 m	1.5	22	ν_aCu–NH_2
		317.6 w	2.1	6	ν_aCu–OOC
244 w	233 w	211.6 m	~0	*e*)	δskel

a) Hidden by the $N'D_2$ wagging and torsional bands.
b) Shifts of band center on ^{63}Cu and ^{65}Cu substitution.
c) Shifts on deuteration.
d) ν: stretching; δ: deformation.
e) Not observed, since the corresponding band of $[Cu(asn\text{-}d_4)_2]_n$ is not observed or is hidden by a neighboring band.

The symmetrical modes of the Cu-ligand stretching vibration are expected in this region. The bands caused from these vibrations are expected to be weak and to show small isotope shifts on ^{63}Cu and ^{65}Cu substitution, since these vibrations include a small displcement of the Cu atom. Thus, two very weak bands at 514 and 500 cm^{-1}, which display relatively small isotope shifts on ^{63}Cu and ^{65}Cu substitution, as shown in Table 2, may be assigned to symmetrical Cu-ligand stretching vibrations. However, the observed magnitudes of the metal isotope shifts of these two bands is also compatible with their assignment to skeletal deformation vibrations with slight contributions by the Cu-ligand stretching vibrations. Throughout the investigated region, no band assignable to the

Cu-O' stretching vibration was observed. The Cu-O' bond-lengths are too long for their stretching vibrations to be observed in the region above 200 cm^{-1}. The assignments discussed above are summarized together with the isotope shifts in Table II.

As discussed above, it is often dangerous to attempt to identify the Cu-ligand stretching vibrations only by comparing the IR spectra of the complex and the ligand. However, ^{63}Cu and ^{65}Cu substitution is very useful as a means to assign vibrations that include displacement of a Cu atom of a complicated complex such as $[Cu(asn)_2]_n$, although such substitution is ineffective for Cu-ligand stretching vibrations that do not include displacements of a Cu atom. The Cu-ligand stretching frequencies obtained in this study do not agree well with those of the related complexes reported by Walter *et al.*,15-17) and comprehensively by Herlinger *et al.*,18,19) and the results of these authors also differ from each other. Although Walter *et al.* carried out normal coordinate analysis by assuming a monomeric chelate model, it seems desirable to reexamine their assignments by using the metal isotope technique. The Cu-O and Cu-N asymmetrical stretching frequencies of $[Cu(asn)_2]_n$ are lower by about 40 and 80 cm^{-1} than the Cu-O and Cu-N antisymmetric stretching frequencies of *cis*-$Cu(glycine)_2 \cdot H_2O$, respectively, although the Cu-ligand bond-lengths of $[Cu(asn)_2]_n$ and

Cu(glycine)$_2$·H$_2$O are not very different from each other.[9,20] These Cu-glycine stretching frequencies are comparable with those of Cu(glycine)$_2$·2H$_2$O, whose structure was estimated to be *trans*-monomeric by analogy with the structure of Ni(glycine)·2H$_2$O.[14,21] It is of interest that the Cu-ligand stretching frequencies of [Cu(asn)$_2$]$_n$ are also much lower than those of *trans*-Cu(glycine)$_2$·2H$_2$O, which has the same coordinating number and *trans*-structure as [Cu(asn)$_2$]$_n$. This frequency difference may reflected the structure difference between the monomeric and polymeric structure through a complicated vibrational coupling.

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Chapter II

Infrared Spectra of Bis(L-asparaginato)zinc(II)

II-1 Introduction

Since metallo-aminoacid complexes are fundamental compounds of metallo-proteins and -enzymes, it is of interest to elucidate the metal-ligand stretching frequencies of aminoacid complexes. It has been shown in chapter I that the metal isotope technique is very useful to identify the IR absorption bands due to the metal-ligand stretching vibrations of polymeric metallo-aminoacid complexes,[1,2)] such as [bis(L-asparaginato)copper(II)]$_n$, which are also of interest because of their biological activities in cancer chemotherapy, *etc.*[3-5)] In this chapter, the metal isotope technique, ^{64}Zn and ^{68}Zn substitution, has been applied to analyze the IR spectrum of [bis(L-asparaginato)zinc(II)]$_n$. In order to acquire fundamental data relating to biological materials containing zinc, the Zn-ligand stretching vibrations have been assigned by referring to the isotope shifts on *N,N'*-deuteration in addition to those on ^{64}Zn and ^{68}Zn substitution. The assignments appear to be fully consistent with the experimental data and may be useful as a basis for further studies on the binding between zinc and aminoacids.

II-2 Experimental

II-2.1 Materials

Purified L-asparagine monohydrate and *N,N'*-deuterated L-asparagine monohydrate ($asn \cdot H_2O$ and $asn\text{-}d_5 \cdot D_2O$) were obtained by the same manner as described in chapter I. [Bis(L-asparaginato)zinc(II)]$_n$, $[Zn(asn)_2]_n$, was prepared from the purified $asn \cdot H_2O$ and reagent-grade zinc acetate dihydrate in aqueous solution. The IR spectrum of the resulting solid coincided completely with that of the product prepared from $ZnCl_2$ according to Stephens *et al.*6) For the preparation of *N,N'*-deuterated complex, $[Zn(asn\text{-}d_4)_2]_n$, anhydrous zinc acetate was reacted with $asn\text{-}d_5 \cdot D_2O$ in heavy water. The precipitate was filtered, washed with heavy water and dried under reduced pressure. For the preparation of complexes containing zinc isotopes, zinc acetates containing ^{64}Zn and ^{68}Zn, which were prepared from ^{64}ZnO and ^{68}ZnO (Oak Ridge National Lab., USA), were reacted with $asn \cdot H_2O$ or $asn\text{-}d_5 \cdot D_2O$ on a milligram scale. The chemical purity of each complex containing zinc isotopes was checked by comparing its IR spectrum with that of the corresponding complex containing zinc of natural abundance. The isotopic purities were 99.85 % for ^{64}ZnO and 99.00 % for ^{68}ZnO.

II-2.2 Measurements

The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000 - 200 cm^{-1}). The measurements were made with solid samples in Nujol and hexachlorobutadiene (Merck AG., Uvasol) mulls. The frequencies were calibrated by the standard absorptions of polystyrene, indene and water vapor. For measuring small shifts of band centers on ^{64}Zn and ^{68}Zn (^{64}Zn-^{68}Zn) substitution, the scale of the frequency was expanded ten times over the desired frequency region, and the measurements were repeated more than three times to check the reproducibility of the spectra.

The IR spectra in the region above 400 cm^{-1} of $[Zn(asn)_2]_n$ and $[Zn(asn\text{-}d_4)_2]_n$ are shown in Fig. 1, and parts of the expanded spectra in Fig. 2.

II-3 Assignments and Discussion

The region between 4000 and 400 cm^{-1}.

None of the bands in this region show an appreciable isotope shift on ^{64}Zn-^{68}Zn substitution and the bands can be assigned to the vibrations of asparaginates. The spectral patterns of both $[Zn(asn)_2]_n$ and $[Zn(asn\text{-}d_4)_2]_n$ were essentially similar to those of the corresponding Cu

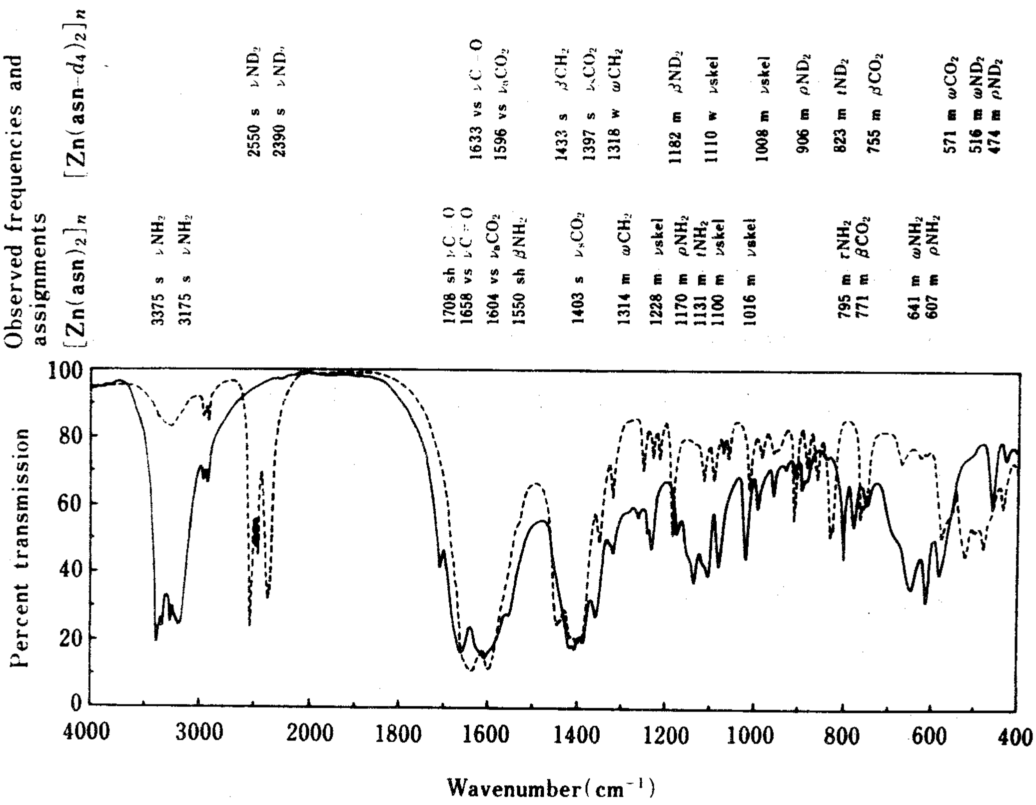

Fig. 1. IR Spectra and Band Assignments of $[Zn(asn)_2]_n$ and $[Zn(asn\text{-}d_4)_2]_n$ in the Region above 400 cm^{-1}

$[Zn(asn)_2]_n$ (——) and $[Zn(asn\text{-}d_4)_2]_n$ (----).

Abbreviations: ν: stretching; δ: deformation; β: bending; ω: wagging; t: twisting; ρ: rocking; τ: torsion; vs: very strong; s: strong; m: medium; w: weak; sh: shoulder.

complexes,$^{1)}$ although differences of coordination and hydrogen bonding between the Cu and the Zn complexes produce small variations in the IR frequencies and intensities. Taking account of these variations, all the bands in this region were assigned to individual vibrations of asparaginates by referring to the assignments of the Cu complexes and the isotope shifts on *N,N'*-deuteration. The assignments of main bands are summarized in Fig. 1.

The region between 400 and 200 cm^{-1}.

According to the X-ray analysis,$^{6)}$ the zinc atom is in a tetragonally distorted octahedral environment constructed by coordination of a carboxylic oxygen (O) and the α-amino nitrogen from each asparaginate with bridges of carboxylic oxygens (O') from neighboring asparaginates. In this environment, the six metal-ligand stretching vibrations are all infrared-active. However, since two Zn-O' bonds are too long for their stretching vibrations to be observed in the region above 200 cm^{-1}, two Zn-O and two Zn-N stretching vibrations can be expected in this region.

In the IR spectrum of $[Zn(asn)_2]_n$ containing zinc of natural abundance, six bands are observed at 387, 371, 301, 265, 244 and 226 cm^{-1} in this region. The band centers of the 301, 265 and 244 cm^{-1} bands show an appreciable isotope shift on

^{64}Zn-^{68}Zn substitution, and they are undoubtedly assigned to the Zn-ligand stretching vibrations including displacement of the zinc atom. On *N,N'*-deuteration, the 387, 371 and 226 cm^{-1} bands are replaced by bands at 350, 334 and 216 cm^{-1}, respectively, whereas the zinc isotope-sensitive bands show a small isotope shift. These isotope shifts on *N,N'*-deuteration indicate that the Zn-O stretching vibrations are probably not localized. By analogy with $[Zn(glutamate)\cdot(H_2O)]_n\cdot(H_2O)_n$,2) it is reasonable to assume that two Zn-O and two Zn-N stretching vibrations couple with one another to produce complicated vibrations which can be classified into relatively asymmetrical and symmetrical vibrations for the zinc atom, although one of the Cu-O' stretching vibrations can probably be regarded as playing a role in this coupling as an additional

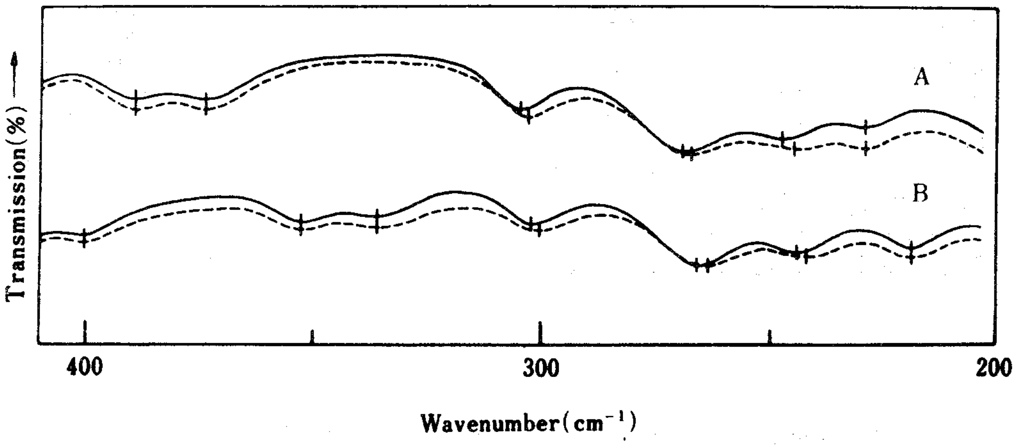

Fig. 2. Expanded IR Spectra of $[Zn(asn)_2]_n$ and $[Zn(asn\text{-}d_4)_2]_n$ in the Region between 410 and 200 cm^{-1}

A: $[^{64}Zn(asn)_2]_n$ (——) and $[^{68}Zn(asn)_2]_n$ (----); B: $[^{64}Zn(asn\text{-}d_4)_2]_n$ (——) and $[^{68}Zn(asn\text{-}d_4)_2]_n$ (----).

vibration. Since the symmetrical vibration is expected to contain a very small displacement of the zinc atom, it probably shows a small shift or no shift on ^{64}Zn-^{68}Zn substitution, in contrast to a large shift on *N*,*N*'-deuteration. Accordingly, three zinc isotope-sensitive bands at 301, 265 and 244 cm^{-1} were assigned to the relatively asymmetrical Zn-ligand stretching vibrations. A symmetrical stretching band was assumed to be missing or to be one of the *N*,*N*'-deuteration sensitive bands at 387, 371 and 226 cm^{-1}. The assignments discussed above are summarized in Table I together with observed frequencies and isotope shifts.

TABLE I. Infrared Frequencies, Isotope Shifts and Assignments of $[Zn(asn)_2]_n$ and $[Zn(asn\text{-}d_4)_2]_n$ in the Region between 400 and 200 cm^{-1}

$[^{64}Zn(asn)_2]_n$ [a]	$\Delta\nu_m$ [b]	$[^{64}Zn(asn\text{-}d_4)_2]_n$ [a]	$\Delta\nu_m$ [b]	$\Delta\nu_h$ [c]	Assignment [d]
387.5 w	0	350.8 w	0	37	δskel [e]
371.4 w	0	335 sh	—	36	δskel [e]
302.1 m	2.1	300.1 m	2.0	2	ν_a Zn-ligand
266.2 m	2.1	262.8 m	2.3	3	ν_a Zn-ligand
244.6 w	2.5	241.0 w	2.0	4	ν_a Zn-ligand
266.0 w	0	215.5 w	0	10	δskel [e]

a) m: medium; w: weak; sh: shoulder.
b) Shifts of band center on ^{64}Zn-^{68}Zn substitution.
c) Shifts on deuteration.
d) ν: stretching; δ: deformation.
e) One of these bands may be assigned to ν_s Zn-ligand.

The frequency range of the metal-ligand stretching vibrations of $[Zn(asn)_2]_n$ is lower by about 50 cm^{-1} than those of $[Cu(asn)_2]_n$.[1] In spite of a difference in coordination structure, the frequency difference between Cu and Zn asparaginates is consistent with that of Cu and Zn glutamates, which are isostructural with each other.2) This result suggests that the structure difference does not much affect the frequency difference between the Cu- and Zn-ligand stretching vibrations, but the stretching force constant may do so. It is of interest that strong coupling among the Zn-ligand stretching vibrations exists in $[Zn(asn)_2]_n$, in contrast to the case of $[Cu(asn)_2]_n$.1) However, the coupling among the Zn-ligand stretching vibrations is not general for the zinc-aminoacid complexes.

The Zn-ligand stretching frequencies of $[Zn(asn)_2]_n$ are consistent with those of $[Zn(glutamate)\cdot(H_2O)]_n\cdot(H_2O)_n$2) and $[Zn(glycinate)_2\cdot(H_2O)]_n$.7,8) Considering that the coupling discussed above is a result of the frequency similarity among the Zn-N and the Zn-O stretching vibrations, it can be concluded that the Zn-O stretching vibrations appear in the region between 330 and 230 cm^{-1} for the polymeric aminoacid complexes. In contrast with the assignment in this chapter, Jackovitz *et al.*9,10) carried out normal coordinate analysis and assigned the bands around 160 cm^{-1} to the Zn-O stretching vibrations in their comprehensive studies of metallo-aminoacid complexes. The conclusion in this chapter suggests that the stretching force constant for Zn-O bonds is probably much larger than that assumed by them.

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Chapter III

Infrared Spectra of Copper and Zinc Glutamate Dihydrates

III-1 Introduction

Complexes containing glutamic acid have centered much interest because of their biological properties,$^{1-3)}$ and have been investigated by various methods.$^{4-16)}$ However, it seems to be rather difficult to analyze the IR spectra of metal glutamates simply by comparison with those of related complexes and the ligand molecule, since they frequently have a complicated polymeric structure. This may be one of the reasons why the IR spectra of the metal glutamates have been investigated in less detail than their X-ray analyses$^{6-10)}$ and ESR spectra.$^{11-16)}$ On the other hand, it has been shown in the previous chapters for complicated polymeric complexes, copper and zinc asparaginates, that the metal isotope technique is very useful to assign the vibrations including displacement of the metal.$^{17)}$

In this chapter, the IR spectra of polymeric copper and zinc glutamate dihydrates, whose structures resemble each other, were investigated by the metal isotope technique in order to study the difference of metal-ligand stretching vibrations between the copper and zinc complexes. The metal isotope shifts indicated that the Cu-ligand stretching frequencies are higher by about 50-100 cm^{-1} than the Zn-ligand stretching frequencies, and the isotope shifts on *N*,*O*-deuteration suggested that the vibrational modes of the metal-ligand stretching vibrations of the Cu complex are very different from those of the Zn complex.

III-2 Experimental

III-2.1 Materials

Commercially available monosodium L-glutamate monohydrate (Na·glu, Ishizu Seiyaku) was purified several times by recrystallization from a mixture of water and ethanol. *N*,*O*-Deuterated monosodium L-glutamate monohydrate (Na·glu-d_5) was obtained from the purified Na·glu by the usual exchange reaction with heavy water (Merck, AG., 99%). Copper and zinc glutamate dihydrates (Cu·glu and Zn·glu) were prepared from the Na·glu and the corresponding metal acetates. The IR spectra of these complexes coincided completely with those of the complexes prepared from cupric nitrate or zinc oxide according to the method of Grammaccioli *et al.*[6, 7] The yield from the acetate was higher than that from the nitrate or the oxide. For the preparation of the *N*,*O*-deuterated complexes (Cu·glu-d_6 and Zn·glu-d_6), anhydrous cupric or zinc acetate was reacted with the Na·glu-d_5 in heavy water. The precipitate was filtered, washed with heavy water and dried over silica gel. For the preparation of the complexes containing metal isotopes, ^{63}CuO, ^{65}CuO, ^{64}ZnO and ^{68}ZnO (Oak Ridge National Lab., USA) were converted into the corresponding cupric and zinc acetates by reaction with dilute acetic acid on a milligram scale. ^{63}Cu·glu, ^{65}Cu·glu, ^{64}Zn·glu and ^{68}Zn·glu and their *N,O*-deuterated complexes were obtained from corresponding acetates by similar methods. The chemical purity of each complex containing the metal isotope was checked by comparing its IR spectrum with that of the complex containing metal of natural abundance. The isotopic purities were 99.89 % for ^{63}CuO, 99.70 % for ^{65}CuO, 99.85 % for ^{64}ZnO and 99.30 % for ^{68}ZnO.

III-2.2 Measurements

The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000 - 200 cm^{-1}). The measurements were made with solid samples in Nujol and hexachlorobutadiene (Merck, AG., Uvasol) mulls. The frequencies were calibrated by use of the standard absorptions of polystyrene, indene and water vapor. For measuring small shifts of band centers due to the metal isotope substitutions (^{63}Cu-^{65}Cu and ^{64}Zn-^{68}Zn), the frequency scale was expanded ten-fold over the desired frequency region, and the measurements were repeated at least three times to check the reproducibility of the spectra.

The IR spectra in the region above 400 cm^{-1} of Cu·glu, Zn·glu and their *N,O*-deuterated analogues are shown in Fig. 1 and parts of the expanded spectra are shown in Fig. 2.

Ⅲ-3 Assignments and Discussion

The region above 500 cm^{-1}.

All the bands of Cu•glu and Zn•glu in this region should be assigned to vibrations of glutamate since no band in this region shows an appreciable isotope shift on metal isotope substitutions. According to the X-ray analyses,[6,7] glutamates in both Cu•glu and Zn•glu take an extended configuration and the bond distances and angles resemble each other except for one of the COO$^-$ groups. As expected from this similarity, the IR spectra of Cu•glu and Cu•glu-d_6 are essentially similar to

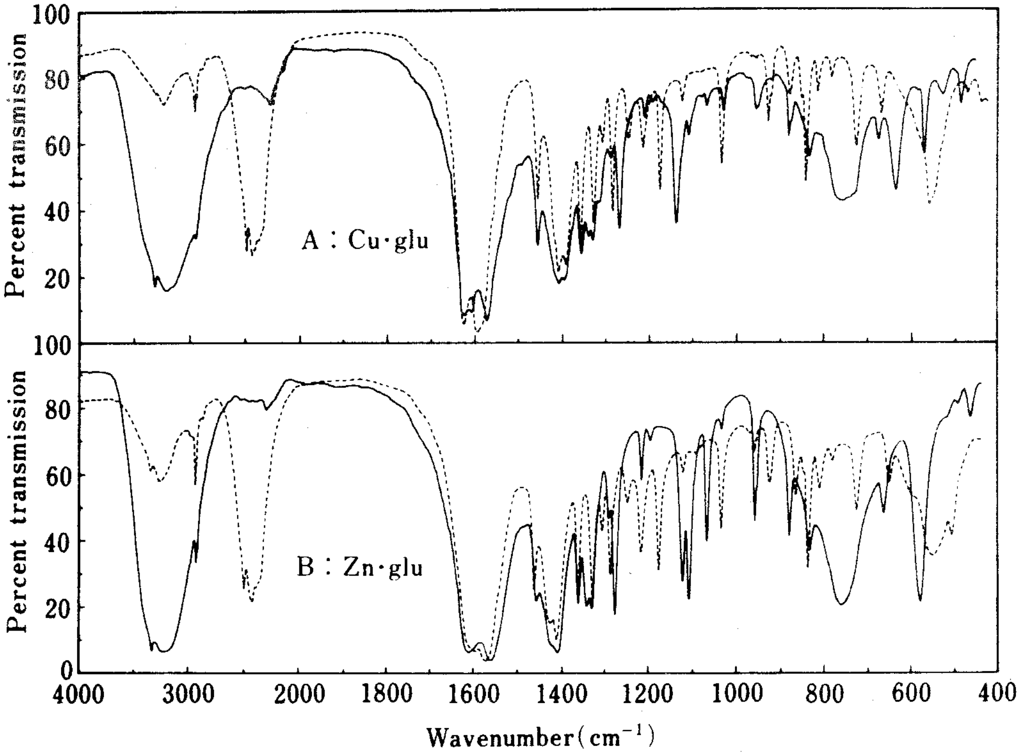

Fig. 1. IR Spectra of Cu·glu and Zn·glu in the Region above 400 cm^{-1}
A: Cu·glu (——) and Cu·glu-d_6 (----); B: Zn·glu (——) and Zn·glu-d_6 (----).

those of Zn•glu and Zn•glu-d_6, as shown in Fig. 1. However, it should be mentioned that the shapes of some bands of Cu•glu, for example the NH_2 and the OH_2 wagging bands, are different from those of Zn•glu because of small differences of hydrogen bonding. With attention to these differences, the absorptions

TABLE I. Infrared Frequencies and Assignments for Cu·glu, Cu·glu-d_6, Zn·glu and Zn·glu-d_6 in the Region above 500 cm^{-1}

Cu·glu[a]	Cu·glu-d_6[a]	Zn·glu[a]	Zn·glu-d_6[a]	Assignments[b]
3310 vs	2480 s	3330 vs	2490 s	$\nu OH_2(OD_2)$ or $\nu NH_2(ND_2)$
3220 vs,b	2430 s	3210 vs,b	2410 s	
2935 sh	2930 w	2930 sh	2920 w	νCH or νCH_2
	2920 w		2900 w	
1623 vs	1622 vs	1610 vs	1611 vs	$\nu_a CO_2$
1570 vs	1594 vs	1573 vs	1565 vs	$\nu_a CO_2$
1607 vs	1174 m	1596 vs	1176 m	$\beta NH_2(ND_2)$
1454 m	1454 m	1456 m	1459 m	βCH_2
1407 s	1410 s	1422 s	1424 s	$\nu_s CO_2$
1393 s	1393 s	1408 s	1410 s	$\nu_s CO_2$
1357 m	1359 m	1359 m	1359 m	δCH
1340 m	1328 m	1340 m	1328 m	δCH
1331 m	1306 w	1328 m	1305 m	ωCH_2
1288 m	1254 m	1285 m	1245 m	ωCH_2
1268 m	1283 m	1272 m	1286 m	νCN
1210 w	1213 m	1207 m	1216 m	$t CH_2$
1192 w	1174 m	1188 w	1176 m	$t CH_2$
1138 m	881 m	1121 m	863 m	$\omega NH_2(ND_2)$
1109 w	843 m	1107 m	835 m	$t NH_2(ND_2)$
1066 w	1123 w	1065 m	1119 w	νskel
1030 w	1034 m	1029 w	1029 m	νskel
958 m	930 m	953 m	957 w	νskel
952 sh	923 sh	950 sh	923 m	νskel
883 m	—[d]	874 m	—[d]	$\rho NH_2(ND_2)$
835 m	816 w	827 m	809 m	ρCH_2
—[c]	784 w	—[c]	778 w	ρCH_2
764 m,b	561 m,b	753 m,b	553 m,b	$\omega H_2O(D_2O)$
—[c]	729 m	—[c]	721 m	βCO_2
678 m	670 m	656 m	649 m	ρCO_2
641 m	—[d]	573 m	—[d]	ωCO_2
574 m	550 sh	512 w	508 sh	δskel
535 w	469 w	488 w	432 w	δskel

a) vs: very strong; s: strong; m: medium; w: weak; vw: very weak; b: broad.
b) ν: stretching; β: bending; δ: deformation; ω: wagging; ρ: rocking; t: twisting.
c) Hidden by the H_2O wagging band.
d) Hidden by the D_2O wagging band.

in this region can be tentatively assigned to individual vibrations by referring to the frequency shifts on *N*,*O*-deuteration and the assignments of related compounds.[18-21] The assignments for Cu·glu, Zn·glu, Cu·glu-d_6 and Zn·glu-d_6 are summarized in Table I together with the observed frequencies and the approximate intensities.

The region between 500 and 200 cm^{-1}.

According to the X-ray analyses,[6,7] Cu·glu and Zn·glu are nearly isostructural, and the principal ligands of both metals are arranged in the form of an approximately square pyramide, including three oxygens and a nitrogen of glutamates and a water molecule. Consequently, five metal-ligand stretching vibrations can be expected to be infrared-active for both Cu·glu and Zn·glu. However, one of the Cu-OOC bonds is too long (2.3 Å) for its stretching vibration to be observed in the region above 200 cm^{-1}, whereas the Zn atom is approximately equidistant from all five ligands. Accordingly, four and five metal-ligand stretching vibrations can be expected for Cu·glu and Zn·glu, respectively, in this region.

For Cu·glu, seven bands are observed at 486, 404, 352, 335, 279, 270 and 232 cm^{-1} in this region, as shown in Fig. 2. By simple comparison between the IR spectra of Na·glu and Cu·glu, it is not possible to estimate which bands can be assigned to

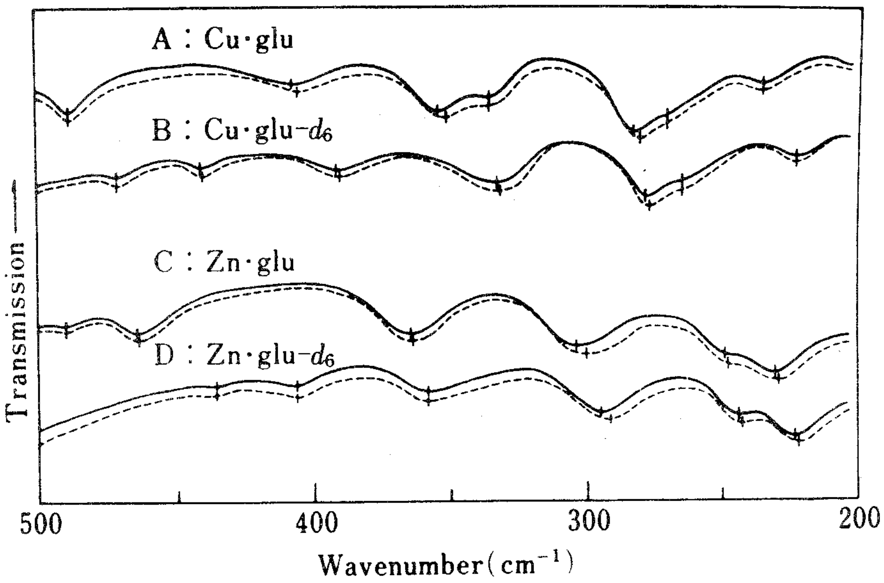

Fig. 2. IR Spectra of Cu·glu and Zn·glu in the Region between 500 and 200 cm^{-1}

A: ^{63}Cu·glu (——) and ^{65}Cu·glu (-----); B: ^{63}Cu·glu-d_6 (——) and ^{65}Cu·glu-d_6 (-----); C: ^{64}Zn·glu (——) and ^{68}Zn·glu (-----); D: ^{64}Zn·glu-d_6 (——) and ^{68}Zn·glu-d_6 (-----).

the Cu-ligand stretching vibrations. The reason is that the skeletal deformation frequencies should be different from those of Na·glu because of the configuration change of glutamate upon complex formation. On ^{63}Cu-^{65}Cu substitution, however, the centers of the 404, 352 and 279 cm^{-1} bands shift to the lower frequency region by about 2 cm^{-1} and these bands can undoubtedly be assigned to vibrations including displacement of the Cu atom. Since the 279 cm^{-1} band remains almost unshifted on *N*,*O*-deuteration, this band can be assigned to a Cu-OOC stretching vibration. In contrast, the 404 and the 352 cm^{-1} bands are replaced by bands at 389 and 329 cm^{-1}, respectively, on *N*,*O*-deuteration, suggesting that the vibrational

TABLE II. Infrared Frequencies, Isotope Shifts and Assignments for Cu·glu and Cu·glu-d_6 in the Region between 500 and 200 cm^{-1}

^{63}Cu·glu[a]	$\Delta\nu_m$[b]	^{63}Cu·glu-d_6[a]	$\Delta\nu_m$[b]	$\Delta\nu_h$[c]	Assignments[d]
486.1 m	0	438.2 w	0.5	48	δskel
404.3 w	1.7	389.8 w	1.0	15	νCu–N or νCu–$OH_2(OD_2)$
353.0 m	2.2	330.0 m	0	23	νCu–N or νCu–$OH_2(OD_2)$
335 sh	~0	[e]	[e]	~5	δskel
280.0 m	2.1	275.8 m	1.2	4	νCu–OOC
270 sh	~0	265 sh	~0	~5	δskel
232.4 w	0	220.6 w	0	12	δskel

a) m: medium; w: weak; sh: shoulder.
b) Shift of band center on ^{63}Cu–^{65}Cu substitution.
c) Shift on *N,O*-deuteration.
d) ν: stretching; δ: deformation.
e) Hidden by a neighboring band.

TABLE III. Infrared Frequencies, Isotope Shifts and Assignments for Zn·glu and Zn·glu-d_6 in the Region between 500 and 200 cm^{-1}

^{64}Zn·glu[a]	$\Delta\nu_m$[b]	^{64}Zn·glu-d_6[a]	$\Delta\nu_m$[b]	$\Delta\nu_h$[c]	Assignments[d]
488.7 vw	0	440.0 vw	0	49	δskel
461.1 m	0.5	403.8 w	0	57	δskel
362.2 m	0.5	356.0 m	0	6	δskel
300.5 m	3.0	291.9 m	2.5	8	νZn-ligand
245 sh	~1	240 sh	~1	~5	νZn-ligand
227.7 m	1.0	220.2 m	1.5	7	νZn-ligand

a) m: medium; vw: very weak; sh: shoulder.
b) Shift of band center on ^{64}Zn–^{68}Zn substitution.
c) Shift on *N,O*-deuteration.
d) ν: stretching; δ: deformation.

modes of these bands include a small displacement of active hydrogen atoms. Accordingly, these bands were assigned to either Cu-OH_2 or Cu-NH_2 stretching vibrations. The 329 cm^{-1} band of Cu·glu-d_6 assigned to the Cu-ND_2 or the Cu-OD_2 stretching vibration shows no appreciable copper isotope shift because of interference of a skeletal deformation band corresponding to the band at 335 cm^{-1} of Cu·glu. No bands assignable to another

Cu-OOC stretching vibration were observed in this region. Probably, this vibration is hidden or includes too small displacement of the Cu atom for the metal isotope shift to be observed.

As shown in Fig. 2, the IR spectrum of Zn·glu is similar to that of Cu·glu except for the strong band at 227 cm^{-1}. It seems reasonable that the assignment for Cu·glu may be transferrable to Zn·glu. However, the shifts of Zn·glu bands on *N*,*O*-deuteration are very different from those of Cu·glu bands in this region, as shown in Fig. 2. This difference suggests that the vibrational modes in the region are varied by changing the metal from Cu to Zn and thus that the assignments for Cu·glu are not transferrable to Zn·glu. Shifts on ^{64}Zn-^{68}Zn substitution are appreciable for bands at 299, 245 and 227 cm^{-1} of Zn·glu and at 291, 240 and 220 cm^{-1} of Zn·glu-d_6, as shown in Fig. 2, and these bands were assigned to the Zn-ligand stretching vibrations. The frequency shifts of about 5-8 cm^{-1} on *N*,*O*-deuteration are less than a half of those of the Cu-OH_2 and the Cu-NH_2 stretching bands of Cu·glu. Accordingly, these three bands of Zn·glu were assigned to vibrations caused by complicated coupling of the Zn-OOC stretching vibrations with the Zn-OH_2 and/or the Zn-NH_2 stretching vibrations. It was difficult to identify other Cu-OOC stretching bands without any additional isotope labels.

The assignments discussed above are summarized in Tables II and III together with the observed metal isotope shifts.

As described above, it seems strange that the modes of coupling among the metal-ligand stretching vibrations are different between Cu·glu and Zn·glu, even though the complexes are nearly isostructural.$^{6,7)}$ Considering only metal-ligand bonds of around 2.0 Å, Cu·glu can be approximated as a square planar coordination structure including two oxygens of glutamate, whereas Zn·glu can be regarded as a square pyramid including three oxygens. In this approximation, three Zn-O and two Cu-O stretching vibrations give MX_3 and MX_2 type vibrational modes, respectively. This may cause the difference of coupling among the Cu-ligand and the Zn-ligand stretching vibrations. In particular, it is of interest that the Zn-O and the Zn-N stretching vibrations are not localized, but couple with one another. Accordingly, when the metal-ligand stretching vibrations are empirically assigned on alternating the metals in the complexes, care is necessary regarding changes of the vibrational modes.

The Cu-OOC stretching frequency of Cu·glu is lower by about 50 cm^{-1} than the Cu-OOC antisymmetric stretching frequencies of *trans*-$^{23)}$ and *cis*-bis-glycinato copper complexes$^{23)}$ and is comparable with that of polymeric $[Cu(asparaginate)_2]_n$.$^{17)}$ This may indicate that polymerization through bridges of ligand molecules plays a role in decreasing the Cu-OOC stretching frequency, as pointed out in chapter I.

In the case of Zn·glu, since the Zn-ligand stretching vibrations couple with one another, it is difficult to compare the individual Zn-ligand stretching frequencies with the localized Zn-O and Zn-N stretching frequencies of related complexes. However, the frequency range of the Zn-ligand stretching bands is comparable with Zn-O stretching frequencies of polymeric *trans*-bis(glycinato)zinc(II) monohydrate investigated by means of zinc, oxygen and nitrogen isotope substitutions,24) and is apparently different from those of DL-alanine and DL-leucine zinc complexes studied by the method of normal coordinate analysis on the basis of a monomeric model.25,26) Since the assignments and structures of the latter two complexes are not definitive, this frequency difference cannot be simply concluded to be due to the differences between polymeric and monomeric structures.

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Chapter IV

Infrared Spectra of *trans*- and *cis*-Bis(D-alaninato)copper(II)

IV-1 Introduction

The copper alaninate complex is known to take a *trans* or a *cis* conformation$^{1,2)}$ as shown in Fig. 1, and its vibrational spectrum is of much interest in relation to the *trans*-*cis* isomerism of the square planar metal complexes. Jackovitz *et al.* made vibrational assignments for bis-DL-alaninatocopper on the basis of the normal coordinate analysis by using a *trans* planar model neglecting hydrogen atoms.$^{3)}$ Herlinger *et al.* tried to identify the differences of the Cu-ligand stretching vibrations between the *trans* and the *cis* complexes.$^{4)}$ Recently, Percy and Stenton assigned the Cu-ligand stretching bands of *trans*-bis-L-alaninatocopper by means of ^{18}O- and ^{15}N-substitutions$^{5)}$ and corrected the assignments of the previous authors. However, no comprehensive investigation has yet been done to resolve the disagreements of the assignments among all the previous reports. In particular, no work has been carried out on the *N*-deuterated complexes and the *cis* complex containing isotopes in order to assign the Cu-ligand stretching vibrations.

This chapter deals with IR spectra of *trans*- and *cis*-bis-D-alaninatocopper and their *N*-deuterated complexes, with the aim of clarifying how the Cu-ligand stretching vibrations are affected by the *trans-cis* isomerism. The Cu–ligand stretching vibrations were assigned unambiguously by using the metal isotope technique. The normal coordinate analysis of the *trans* and the *cis* complexes was carried out by taking account of both the intra- and intermolecular forces to confirm the empirical assignments.

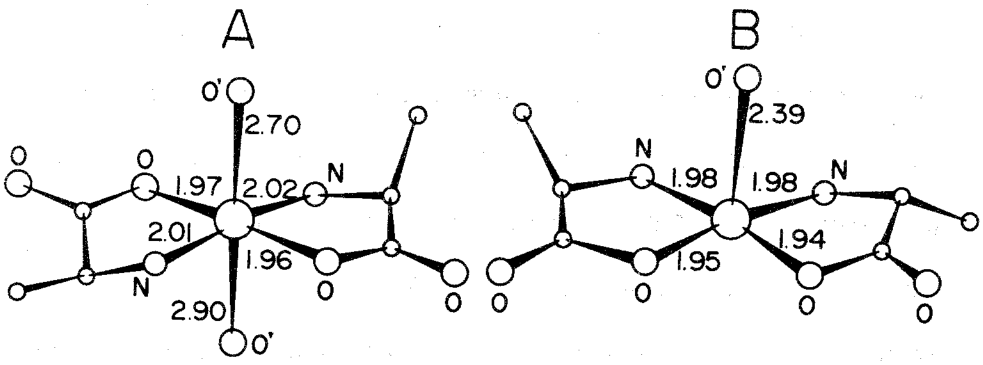

Fig. 1 Structures and Bond-lengths[1,2] of t-Cu(ala)$_2$ (A) and c-Cu(ala)$_2$ (B)

IV-2 Experimental

IV-2.1 Materials

Commercially available D-alanine (D-ala, Ishizu Seiyaku) was recrystallized several times from a mixture of water and ethanol. *N*-Deuterated D-alanine (D-ala-d_3) was obtained from the purified D-ala by the usual exchange reaction with heavy water (Merck, AG., 99%). *trans*-Bis(D-alaninato)copper(II), *t*-Cu(ala)$_2$, was prepared from the purified D-ala according to the method of Dijkstra.1) For the preparation of *N*-deuterated *trans*-complex, *t*-Cu(ala-d_2)$_2$, anhydrous cupric acetate was reacted with D-ala-d_3 in heavy water. The complexes containing copper isotopes were obtained from cupric acetates which were prepared from ^{63}CuO and ^{65}CuO (Oak Ridge National Lab., USA) in the same manner as described in chapter I. About 20 mg of each complex was obtained. *cis*-Bis(D-alaninato)copper(II) and its isotopic complexes, *c*-Cu(ala)$_2$, *etc*., were prepared by annealing the corresponding *trans*-complex suspended in water or heavy water for three days on a boiling water bath.6)
The isotopic purities were 99.89 % for ^{63}CuO and 99.70 % for ^{65}CuO.

IV-2.2 Measurements

The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000 - 200 cm^{-1}). The measurements were made with solid samples in Nujol and hexachlorobutadiene (Merck, AG., Uvasol) mulls. The frequencies were calibrated by the standard absorptions of polystyrene, indene and water vapor. For measuring small shifts of band centers on ^{63}Cu and ^{65}Cu substitution (^{63}Cu-^{65}Cu), the scale of the frequency was expanded ten times over the desired region, and the measurements were repeated at least three times to check the reproducibility of the spectra.

The IR spectra in the region between 4000 and 400 cm^{-1} are shown in Fig. 2 and parts of the expanded spectra in Fig. 3. The observed frequencies are listed in Tables I and II together with approximate intensities, assignments and calculated frequencies.

IV-3 Normal Coordinate Analyses

According to the X-ray analyses,$^{1,2)}$ both the *trans*- and *cis*-complexes take a polymeric structure chained by a weak bond between copper and one of the carboxylate oxygen atoms (O') of the neighboring alaninates as shown in Fig. 1. The optical active normal frequencies of these chain molecules were calculated by using a program newly written by Machida in this work for vibrational analysis of the crystals of molecular and ionic complexes. The method of Harada and Shimanouchi$^{7)}$ was adopted by taking account of the effect of the first derivatives of the intermolecular potential with respect to the interatomic distances. The contribution of the Coulombic forces between the atomic charges was treated by Eward's method as described by Hiraishi.$^{8)}$ The calculations were carried out on a FACOM M-190 computer at the Data Processing Center of Kyoto University and an ACOS 1000 computer at Okayama University Computer Center. The CPU time for calculating a set of optical active frequencies of *trans*- or *cis*-$Cu(ala)_2$ was 13 seconds in the ACOS 1000 computer. Assuming the bond-lengths r_{CH}=1.080 and r_{NH}=1.020 Å, the coordinates of *cis*-$Cu(ala)_2$ were constructed on the basis of the X-ray analysis by Gillard *et al.*$^{2)}$ and partially modified coordinates$^{1,9)}$ of $Cu(L\text{-}ala)_2$ were used for *t*-$Cu(ala)_2$. A modified Urey-Bradley force field was used with a few valence type constants of torsional and out-of-plane bending coordinates. The force constants related to alaninate were initially transferred from L-alanine crystal.10) The transferability of these constants was sufficiently good that the initial calculation gave useful clues to the assignments. The constants related to the Cu-ligand bonds were taken from those reported by Inomata *et al.*11) The stretching constant, K(CuO'), was used for weak Cu-O' bonds and was assumed to be 0.10 mdyn/Å. The bending and the repulsive constants concerned to the CuO' bonds were initially assumed to be zero. The force constants related to the Cu atom were mainly adjusted to improve the frequency fit, and an interaction constant between the C=O stretching and the CH deformation vibrations was introduced to reproduce the ^{18}O-induced shifts reported by Percy *et al.*5) The final values of the adjusted intramolecular force constants are listed in Table III.

Initially, the calculation were carried out by using only the intramolecular force constants (calculation I). Later, the intrachain intermolecular forces were taken into account in calculation II. The interchain forces were neglected by taking account of only two of four asymmetric units in a unit cell of the *cis* complex. By referring to the previous treatments of aminoacid,10,12-15) the intermolecular potential was assumed to be the sum of the exp-6 type nonbonded atom-

atom interaction terms, the Lippincott type hydrogen-bond stretching terms and the Coulomb interaction terms. The potential parameters for these terms are the same as those used for α-glycine-*C*-d_2 and DL-alanine-α,β-d_4 crystals.[13)] In calculating the Coulomb interaction terms, the atomic charges were estimated by the CNDO/II calculation in which the Cu atom of $Cu(ala)_2$ was replaced by an Mg atom. The limits for the direct and the reciprocal lattice sums were taken as 20.0 Å and 0.2 Å, respectively, with the convergence parameter K = 0.2.

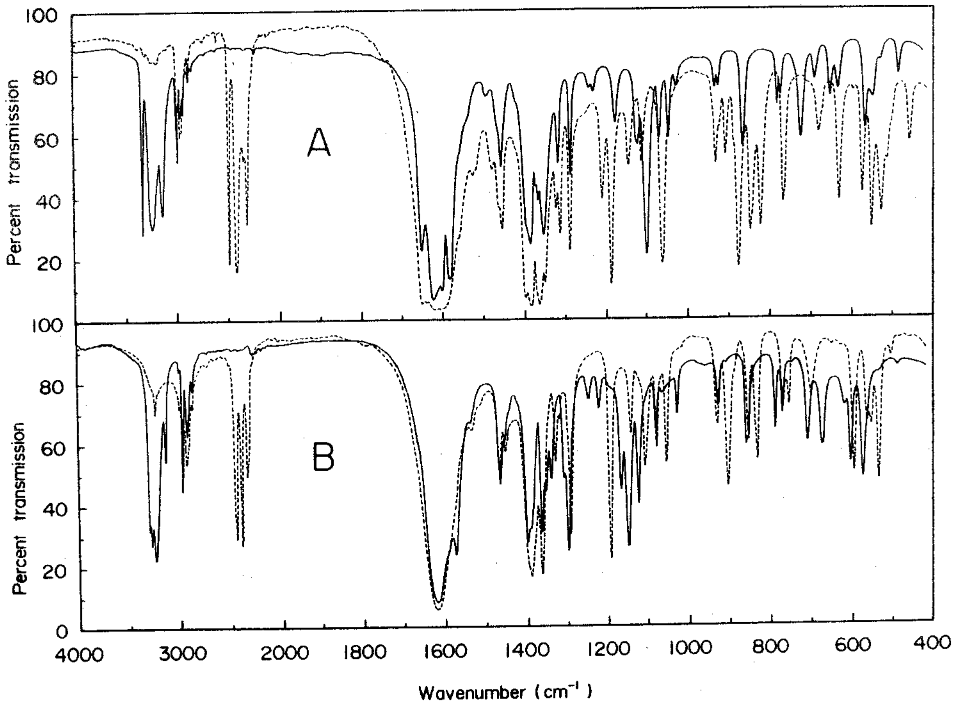

Fig.2 IR Spectra of *t*-$Cu(ala)_2$, *t*-$Cu(ala\text{-}d_2)_2$, *c*-$Cu(ala)_2$ and *c*-$Cu(ala\text{-}d_2)_2$ in the Region above 400 cm^{-1},
A : *t*-$Cu(ala)_2$ (———) and *t*-$Cu(ala\text{-}d_2)_2$ (------);
B : *c*-$Cu(ala)_2$ (———) and *c*-$Cu(ala\text{-}d_2)_2$ (------).

IV-4 Assignments and Discussion

The region 4000 - 500 cm^{-1}.

All the bands of *t*-Cu(ala)$_2$, *t*-Cu(ala-*d*$_2$)$_2$, *c*-Cu(ala)$_2$ and *c*-Cu(ala-*d*$_2$)$_2$ in this region show no appreciable shift on ^{63}Cu-^{65}Cu substitution and can be assigned to the vibrations including no displacement of the Cu atom. By referring to the frequency shifts on *N*-deuteration and the assignments of previous authors,[3-5,10,11,16) the bands in this region were assigned to individual vibrations of alaninates. As shown in Tables I and II, the agreement of the calculated and the observed frequencies was satisfactory throughout the four complexes in spite of such a crude approximation as to use the same intramolecular force constants for the *trans* and the *cis* complexes. The calculated L-matrices reveal that the COO bending and rocking frequencies of alaninates, a' and b', are larger than those of a" and b", as opposed to the COO wagging frequencies. This result indicates that the conformational differences of alaninates are reflected sensitively in the COO deformational frequencies.

Appreciable ^{15}N- and ^{18}O-induced shifts were reported for *t*-Cu(ala)$_2$ by Percy *et al.*5) As shown in Table I, the calculated ^{15}N-induced shifts agreed well with the reported shifts in this region with the use of the simple Urey-Bradley force field, while some of the calculated ^{18}O-induced shifts did not follow the reported shifts in the absence of the

Table I Observed and Calculated Frequencies, ^{15}N-Induced Shifts, ^{18}O-Induced Shifts and Assignments for *trans*-Cu(D-alaninate)$_2$ and its *N*,*N'*-Deuterated Analogues in the Region between 4000 and 500 cm^{-1}

t-Cu(ala)$_2$						
Obs.a)	$\Delta^{15}N$ Obs.5)	$\Delta^{18}O$ Obs.5)	Calc.b)	$\Delta^{15}N$ Calc.	$\Delta^{18}O$ Calc.	Assignmentsc)
3281 s	-d)	-d)	3292 a'	8.9	0.0	$\nu_a NH_2$
3276 s	-d)	-d)	3286 a"	8.8	0.0	$\nu_a NH_2$
3240 s	-d)	-d)	3232 a'	4.6	0.0	$\nu_s NH_2$
3133 s	-d)	-d)	3230 a"	4.7	0.0	$\nu_s NH_2$
2973 m	-d)	-d)	2976 a"	0.0	0.0	$\nu_s CH_3$ or $\nu_d CH_3$ or νCH
			2938 a'	0.0	0.0	
2924 m	-d)	-d)	2896 a'	0.1	0.0	
			2873 a'	0.0	0.0	
			2872 a"	0.0	0.0	
			2869 a"	0.0	0.0	
2868 m	-d)	-d)	2790 a'	0.0	0.0	
			2778 a"	0.1	0.0	
1619 vs	2	21	1643 a'	0.2	18.0	$\nu_a CO_2$
			1633 a"	0.2	22.9	$\nu_a CO_2$
1573 vs	3	e)	1621 a'	3.1	4.5	βNH_2
			1573 a"	3.2	0.3	βNH_2
1463 m	-d)	-d)	1499 a'	0.2	0.1	$\delta_d CH_3$
			1457 a"	0.0	0.0	$\delta_d CH_3$
1452 sh	e)	e)	1454 a"	0.1	0.1	$\delta_d CH_3$
			1450 a'	0.1	0.1	$\delta_d CH_3$
1395 s	e)	-d)	1380 a'	0.6	22.8	$\nu_s CO_2$
1364 s	1.5	10	1373 a"	0.1	22.2	$\nu_s CO_2$
1387 sh	-d)	-d)	1388 a"	0.3	3.9	$\delta_s CH_3$
			1363 a'	0.4	4.6	$\delta_s CH_3$
1306 w	e)	9	1348 a"	1.6	10.5	δCH
1296 s	1.5	13	1338 a'	1.0	11.6	δCH
1354 sh	e)	e)	1306 a"	2.1	1.9	δCH
1339 m	2	e)	1300 a'	1.6	1.9	δCH
1245 w	e)	e)	1248 a'	1.0	0.3	$t NH_2$
1220 w	e)	2	1213 a"	2.0	0.6	$t NH_2$
1165 m	6	4.5	1161 a"	5.8	1.2	ωNH_2
1149 s	5	4.5	1150 a'	7.3	1.5	ωNH_2
1119 s	6.5	1.5	1138 a'	4.3	1.6	νCN
			1114 a"	5.2	1.6	νCN
1078 m	3	2.5	1043 a'	0.9	5.9	ρCH_3
1026 m	2	2.5	1026 a"	0.1	4.7	ρCH_3
970 vw	-d)	-d)	981 a"	0.3	1.6	ρCH_3
			972 a'	0.3	0.7	ρCH_3
925 m	4.5	5.5	913 a"	2.9	5.1	$\nu skel$
			903 a'	2.7	4.5	$\nu skel$
856 m	3.5	-d)	878 a"	2.1	12.5	$\nu skel$
850 m	2.5	-d)	850 a'	4.2	17.2	$\nu skel$
786 m	e)	8	775 a'	1.0	6.4	ωCO_2
767 m	e)	5	750 a"	0.1	6.4	ωCO_2
706 m	1.5	11	721 a"	2.3	12.9	βCO_2
618 w	-d)	-d)	623 a'	2.8	8.9	βCO_2
672 m	5	2	720 a'	3.0	0.2	ρNH_2
			677 a"	4.9	0.3	ρNH_2
602 m	2.5	12	571 a'	9.0	8.6	ρCO_2
571 m	7.5	7	557 a"	7.3	11.6	ρCO_2
562 sh	-d)	-d)	518 a'	4.1	13.1	$\delta skel$

t-Cu(ala-d_2)$_2$		
Obs.a)	Calc.b)	Assignmentsc)
2970 m	2976 a'	$\nu_s CH_3$ or $\nu_d CH_3$ or νCH
	2938 a"	
2931 m	2898 a'	
	2873 a'	
	2872 a"	
	2869 a"	
2867 m	2790 a'	
	2778 a"	
2450 s	2424 a'	$\nu_a ND_2$
2405 s	2418 a"	$\nu_a ND_2$
2345 s	2338 a'	$\nu_s ND_2$
	2337 a"	$\nu_s ND_2$
1619 vs	1642 a'	$\nu_a CO_2$
	1632 a"	$\nu_a CO_2$
1461 m	1503 a'	$\delta_d CH_3$
	1457 a"	$\delta_d CH_3$
1447 w	1454 a"	$\delta_d CH_3$
	1450 a'	$\delta_d CH_3$
1385 s	1377 a'	$\nu_a CO_2$
	1373 a"	$\nu_a CO_2$
1390 sh	1386 a"	$\delta_s CH_3$
	1362 a'	$\delta_s CH_3$
1358 s 1326 m 1288 m	1336 a"	δCH
	1330 a'	δCH
	1264 a'	δCH
	1246 a"	δCH
1190 s	1203 a'	βND_2
	1171 a"	βND_2
1141 m	1118 a'	νCN
	1101 a"	νCN
1107 m	1085 a'	ρCH_3
1076 m	1058 a"	ρCH_3
1050 m	1047 a"	ρCH_3
	1025 a'	ρCH_3
926 m	930 a"	$t ND_2$
	919 a'	$t ND_2$
905 m	910 a"	$\nu skel$
	900 a'	$\nu skel$
853 m	878 a'	ωND_2
	869 a"	ωND_2
830 m	839 a'	$\nu skel$
	824 a"	$\nu skel$
765 m	759 a'	ωCO_2
751 m	747 a"	ωCO_2
700 m	706 a"	βCO_2
596 m	609 a'	βCO_2
563 m	544 a'	ρND_2
533 m	520 a"	ρND_2
553 m	565 a"	ρCO_2
	553 a'	ρCO_2
503 vw	497 a'	$\delta skel$

a) vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

b) calculation II, species : A, a' and a" (see Fig. 1).

c) ν: stretching; β: bending; δ: deformation; ω: wagging; ρ: rocking; *t*: twisting.

d) not reported.

e) shifted less than 1.5 cm^{-1}.

Table II Observed and Calculated Frequencies and Assignments for *cis*-Cu(D-alaninate)$_2$ and its *N*,*N'*-Deuterated Analogues in the Region between 4000 and 500 cm^{-1}

c-Cu(ala)$_2$		Assignments[c]	*c*-Cu(ala-d_2)$_2$		Assignments[c]
Obs.[a]	Calc.[b]		Obs.[a]	Calc.[b]	
3325 s	3263 b'	$\nu_a NH_2$	2990 m	2960 b"	
3230 s	3260 b"	$\nu_a NH_2$	2960 m	2958 b'	
3120 s	3205 b'	$\nu_s NH_2$	2950 m	2887 b"	$\nu_s CH_3$ or
	3201 b"	$\nu_s NH_2$		2884 b"	$\nu_d CH_3$ or
2980 m	2960 b'		2930 w	2882 b'	νCH
2950 m	2958 b"			2871 b'	
2920 m	2887 b"	$\nu_s CH_3$ or	2880 w	2794 b"	
	2884 b"	$\nu_d CH_3$ or		2784 b'	
2880 w	2882 b'	νCH	2480 s	2405 b'	$\nu_a ND_2$
	2871 b'		2410 s	2403 b"	$\nu_a ND_2$
2840 w	2794 b"		2310 w	2320 b'	$\nu_d ND_2$
	2784 b'		2305 s	2318 b"	$\nu_d ND_2$
1652 s	1643 b'	$\nu_a CO_2$	1654 vs	1642 b'	$\nu_a CO_2$
1625 vs	1640 b"	$\nu_a CO_2$	1611 vs	1640 b"	$\nu_a CO_2$
1601 vs	1594 b"	βNH_2		1471 b'	$\delta_d CH_3$
1582 vs	1589 b'	βNH_2	1478 sh	1455 b"	$\delta_d CH_3$
	1471 b'	$\delta_d CH_3$	1452 m	1452 b'	$\delta_d CH_3$
1490 w	1455 b"	$\delta_d CH_3$		1450 b"	$\delta_d CH_3$
1455 m	1452 b'	$\delta_d CH_3$	1383 vs	1371 b"	$\nu_s CO_2$
	1450 b"	$\delta_d CH_3$	1364 vs	1365 b'	$\nu_s CO_2$
1384 s	1370 b"	$\nu_s CO_2$	1397 sh	1381 b'	$\delta_s CH_3$
	1364 b'	$\nu_s CO_2$		1362 b"	$\delta_s CH_3$
1390 sh	1382 b'	$\delta_s CH_3$	1352 s	1326 b"	δCH
	1363 b"	$\delta_s CH_3$	1320 m	1322 b'	δCH
1364 m	1344 b"	δCH	1310 m	1275 b"	δCH
1352 m	1334 b'	δCH	1287 m	1255 b'	δCH
1312 m	1310 b'	δCH	1208 m	1186 b"	βND_2
1284 m	1280 b"	δCH	1187 s	1179 b'	βND_2
1238 w	1261 b"	$t NH_2$	1141 m	1108 b'	νCN
1226 w	1210 b'	$t NH_2$		1101 b"	νCN
1175 m	1144 b"	ωNH_2	1109 m	1073 b"	ρCH_3
	1131 b'	ωNH_2		1060 b'	ρCH_3
1118 m	1125 b"	νCN	1059 m	1045 b'	ρCH_3
1097 s	1114 b'	νCN		1039 b"	ρCH_3
1065 m	1034 b"	ρCH_3	928 m	925 b"	$\nu skel$
1043 m	1022 b'	ρCH_3	905 m	923 b'	$\nu skel$
1024 w	990 b"	ρCH_3	874 m	911 b'	$t ND_2$
	897 b'	ρCH_3		902 b"	$t ND_2$
929 w	920 b'	$\nu skel$	844 m	872 b"	ωND_2
920 w	903 b"	$\nu skel$		864 b'	ωND_2
860 m	873 b'	$\nu skel$	818 m	840 b"	$\nu skel$
	863 b"	$\nu skel$		820 b'	$\nu skel$
778 m	791 b"	ωCO_2	763 m	779 b"	ωCO_2
769 m	779 b'	ωCO_2		773 b'	ωCO_2
720 m	680 b'	ρNH_2	676 m	677 b'	βCO_2
687 m	660 b"	ρNH_2	623 m	626 b"	βCO_2
649 m	693 b'	βCO_2	572 m	524 b'	ρND_2
630 m	625 b"	βCO_2	548 m	503 b"	ρND_2
565 m	555 b'	ρCO_2	525 m	551 b'	ρCO_2
547 m	549 b"	ρCO_2	511 sh	544 b"	ρCO_2
527 sh	516 b"	$\delta skel$	500 sh	483 b"	$\delta skel$

a) vs: very strong; s: strong; m: medium; w: weak; sh: shoulder.

b) calculation II, species : A, b' and b" (see Fig. 1).

c) ν: stretching; δ: deformation; β: bending; ρ: rocking; ω: wagging; *t*: twisting.

interaction constant between the C=O stretching and the CH deformations. In particular, the CH deformation bands around 1300 cm^{-1} show an appreciable ^{18}O-induced shift by about 10 cm^{-1} in contrast to the small calculated shifts. The interaction constant was very effective in reproducing the reported shifts, as shown in Table I.

Table III Force Constants of Modified Urey-Bradley Type and Valence Type

Modified Urey-Bradley type force constants (mdyn/Å)									
K(C-O)	7.35[a]	H(OCO)	0.06	H(CuNC)	0.10[a]	F(OCO)	2.52	F(CuNC)	0.20[a]
K(C-C)	2.00[a]	H(OCC)	0.31	H(CuOC)	0.10[a]	F(OCC)	0.70	F(CuOC)	0.20[a]
K(C-H)	4.20[a]	H(CCN)[b]	0.55[a]	H(HNCu)	0.10[a]	F(CCN)[b]	0.60	F(HNCu)	0.10
K(C-N)	2.67	H(CCN)	0.22[a]	H(OCuN)[b]	0.10[a]	F(CCN)	0.60	F(OCuN)[b]	0.20[a]
K(N-H)	5.50[a]	H(CCC)	0.30[a]	H(OCuN)[c]	0.10[a]	F(CCC)	0.30	F(OCuN)[c]	0.05
K(Cu-N)	0.95[a]	H(CCH)	0.20[a]	H(OCuO)[d]	0.10[a]	F(CCH)	0.40[a]	F(OCuO)[d]	0.05[a]
K(Cu-O)	0.85[a]	H(NCH)	0.25	H(NCuN)[d]	0.10[a]	F(NCH)	0.54	F(NCuN)[d]	0.05[a]
K(Cu-O')	0.10[a]	H(CNH)	0.34	H(O'CuN)	0.05[a]	F(CNH)	0.50	F(O'CuN)	0.05[a]
κ(C)[e]	0.0185	H(HNH)	0.54	H(O'CuO)	0.05[a]	F(HNH)	0.02	F(O'CuO)	0.05[a]
κ(N)[e]	-0.042	H(HCH)	0.44			F(HCH)	0.02		
Valence type force constants (mdyn·Å/rad^2)									
$f(\omega CO_2, \omega CO_2)$	1.92	$f(\tau CC, \tau CC)$	0.05	$f(\tau CN, \tau CN)$	0.05	$f(\nu_s CO_2, \delta CH)$	0.05		

a) refined values.
b) force constants concerning the chelate ring.
c) used for only the *trans* complex.
d) used for only the *cis* complex.
e) mdyn·Å.

The region between 500 and 200 cm^{-1}.

For *t*-Cu(ala)$_2$, eleven bands assignable to the skeletal deformation and the Cu-ligand stretching vibrations are observed in this region. On ^{63}Cu-^{65}Cu substitution, the centers of the three bands at 361, 331 and 320 cm^{-1} shift by an amount between 2-3 cm^{-1} as shown in Fig. 3. These bands obviously arise from the vibrations including displacement of the copper atom. On *N*-deuteration, the 361 cm^{-1} band is replaced by a band at 339 cm^{-1}, while the 331 and 320 cm^{-1} bands shift by less than 10 cm^{-1}. By referring to these isotope shifts, the 361 cm^{-1} band was assigned to the asymmetrical Cu-N stretching vibration and the 331 and 320 cm^{-1} bands to the Cu-O stretching vibrations. The band at 385 cm^{-1} assigned previously to the Cu-O stretching vibration by Percy and Stenton5) can now be assigned to the skeletal deformation vibration including large displacement of carboxylate oxygen atoms, since this band shows no shifts on ^{63}Cu-^{65}Cu substitution and a large shift on ^{18}*O*-substitution. Previously, the band at 488 cm^{-1} was assigned to the Cu-N antisymmetric stretching vibration by Herlinger *et al.*4) and Percy *et al.*5) However, the 488 cm^{-1} band showed a very small isotope shift on ^{63}Cu-^{65}Cu substitution in contrast to a large shift on *N*-deuteration and on ^{15}*N*-substitution. From these isotope shifts, this band can be assigned to the Cu-N symmetric stretching vibration

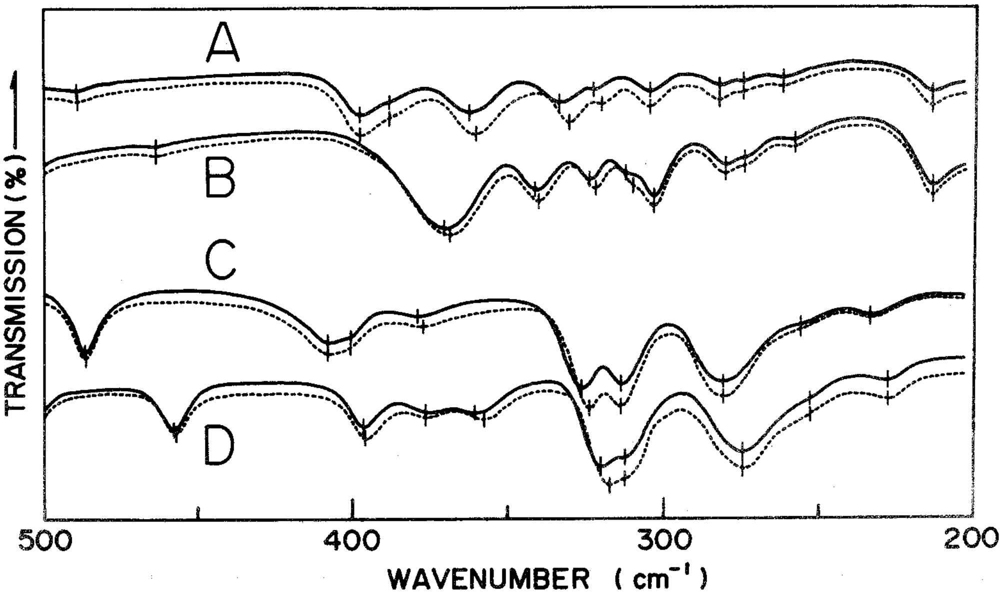

Fig. 3 Expanded IR Spectra of *t*-Cu(ala)$_2$, *t*-Cu(ala-*d*$_2$)$_2$, *c*-Cu(ala)$_2$ and *c*-Cu(ala-*d*$_2$)$_2$ in the Region between 500 and 200 cm^{-1}, A : *t*-^{63}Cu(ala)$_2$ (——) and *t*-^{65}Cu(ala)$_2$ (----); B : *t*-^{63}Cu(ala-*d*$_2$)$_2$ (——) and *t*-^{65}Cu(ala-*d*$_2$)$_2$ (----); C : *c*-^{63}Cu(ala)$_2$ (——) and *c*-^{65}Cu(ala)$_2$ (----); D : *c*-^{63}Cu(ala-*d*$_2$)$_2$ (——) and *c*-^{65}Cu(ala-*d*$_2$)$_2$ (----).

which includes a large displacement of the nitrogen atoms but no appreciable displacement of the copper atom.

For the *cis*-complex, nine bands are observed in this region as shown in Fig. 3. Among them, two bands at 375 and 323 cm^{-1} shift appreciably on ^{63}Cu-^{65}Cu substitution, and could clearly be assigned to the Cu-alaninate stretching vibrations. The 375 cm^{-1} band is replaced by a band at 358 cm^{-1} while the 323

Table IV Observed and Calculated Frequencies, ^{15}N-Induced Shifts, ^{18}O-Induced Shifts, Metal Isotope Shifts and Assignments for *trans*-Cu(D-alaninate)$_2$ and its *N*,*N*'-Deuterated Analogues in the Region below 500 cm^{-1}

t-Cu(ala)$_2$									*t*-Cu(ala-d_2)$_2$					
		$\Delta^{15}N$		$\Delta^{18}O$		Δm c)					Δm c)			Assignments f)
							Calc.					Calc.		
Obs. a)	Calc. b)	Obs. 6)	Calc.	Obs. 6)	Calc.	Obs.	I d)	II e)	Obs. a)	Calc. b)	Obs.	I d)	II e)	
488 w	503	6.5	6.2	6.5	11.3	0.3	0.2	0.2	462 vw	477	0	0.1	0.1	ν_sCu-NH$_2$(ND$_2$)
396 m	436	2	3.0	4	3.2	0.5	0.5	0.0	369 m	{ 417	0.8	{ 1.5	{ 0.0	δskel
385 sh	405	–g)	2.2	–g)	5.2	∿0	0.2	0.2		383		0.5	0.9	δskel
361 m	379	h)	0.6	4.5	6.0	2.0	1.5	0.8	339 m	363	0.7	1.7	0.9	ν_aCu-NH$_2$(ND$_2$)
331 m	346	2	0.9	2.5	3.2	3.0	0.1	1.2	322 w	333	2.0	0.1	2.4	ν_sCu-OOC
320 sh	334	1	0.7	1	4.9	∿3	3.2	3.0	310 sh	329	∿2	1.7	1.2	ν_aCu-OOC
303 m	283	h)	0.4	7	5.6	0	0.0	0.1	301 m	282	0	0.1	0.1	δskel
280 w	275	2	1.6	5	5.9	0	0.1	0.1	278 w	271	0	0.1	0.1	δskel
274 sh	257	–g)	0.7	–g)	3.4	∿0	0.3	0.1	271 sh	255	∿0	0.1	0.1	δskel
213 m	217	1.5	1.1	9	5.6	0	0.0	0.0	211 m	214	0	0.0	0.3	δskel

a) m, medium; w, weak; sh, shoulder.

b) calculation II, species A.

c) Δm, shifts of band center on ^{63}Cu-^{65}Cu substitution.

d) calculation I by using only the intramolecular forces.

e) calculation II by using the intra- and intermolecular forces.

f) ν, stretching; δ, deformation.

g) not reported.

h) shifted less than 1 cm^{-1}.

Table V Observed and Calculated Frequencies, Metal Isotope Shifts and Assignments for *cis*-Cu(D-alaninate)$_2$ and its *N*,*N*'-Deuterated Analogues in the Region below 500 cm^{-1}.

c-Cu(ala)$_2$					*c*-Cu(ala-d_2)$_2$					
		Δm c)					Δm c)			Assignments f)
			Calc.					Calc.		
Obs. a)	Calc. b)	Obs.	I d)	II e)	Obs. a)	Calc. b)	Obs.	I d)	II e)	
483 m	495	0.3	0.4	0.4	456 m	461	0.8	0.3	0.4	ν_sCu-NH$_2$(ND$_2$)
405 m	398	0	0.3	0.2	394 m	378	0.6	1.1	0.8	δskel
400 sh	387	∿0	0.4	0.3	374 vw	366	0	0.9	0.6	ν_sCu-OOC
375 vw	347	1.2	1.6	1.8	358 w	333	2.5	1.5	1.7	ν_aCu-NH$_2$(ND$_2$)
323 m	332	2.6	2.8	2.7	318 m	328	2.5	1.9	2.0	ν_aCu-OOC
312 m	300	0	0.1	0.2	310 sh	300	∿0	0.1	0.1	δskel
278 m	295	0	0.2	0.2	272 m	290	0	0.2	0.2	δskel
231 w	246	0.1	0.1	0.0	225 w	234	0	0.2	0.1	δskel

a) m, medium; w, weak; vw, very weak; sh, shoulder.

b) calculation II, species A.

c) Δm, shifts of band center on ^{63}Cu-^{65}Cu substitution.

d) calculation I by using only the intramolecular forces.

e) calculation II by using the intra- and intermolecular forces.

f) ν, stretching; δ, deformation.

cm^{-1} band remains almost unshifted on *N*-deuteration. Accordingly, the former was assigned to the Cu-N asymmetrical stretching vibration and the latter to the Cu-O asymmetrical stretching vibration. By referring to the calculated frequencies, the bands at 483 and 400 cm^{-1} were tentatively assigned to the Cu-N and the Cu-O symmetrical stretching vibrations, respectively. The frequency shifts of these bands on *N*-deuteration are consistent with this assignments.

The reported ^{18}O- and ^{15}N-induced shifts for *t*-Cu(ala)$_2$ were reproduced well in calculations I and II except for a very small ^{18}O-induced shift of the 320 cm^{-1} band of *t*-Cu(ala)$_2$. This reported shift seems to disagree with any calculated ^{18}O-induced shift. Appreciable isotope shifts on ^{63}Cu-^{65}Cu substitution were predicted only for two frequencies around 340 cm^{-1} in calculation I, whereas three bands showed appreciable shifts in the observed spectrum. In calculation II, however, the intermolecular forces induced a redistribution of the copper isotope shifts among the three bands at 361, 331 and 320 cm^{-1}. For the *cis* complexes, the observed isotope shifts on ^{63}Cu-^{65}Cu substitution were well reproduced by both calculations I and II.

As shown in Tables IV and V, the agreement between the calculated and the observed frequencies in this region was generally good for both the *trans* and *cis* complexes. It seems likely that the intramolecular forces around the Cu atom of the copper alaninate are not sensitive to the change of conformation on *trans-cis* isomerism.

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Chapter V

Infrared Spectra of *trans*-Bis(L-phenylalaninato)copper(II) and α- and β-Bis(DL-phenylalaninato)copper(II)

V-1 Introduction

As fundamental complexes of metallo-proteins and -enzymes, aminoacid-copper complexes have already received considerable attention in relation to their biological activities[1,2] and the role of copper *in vivo*.[3] Among them, isomers of bis(DL-phenylalaninato)copper, Cu(DL-phe)$_2$, have been structurally investigated by means of ESR[4] and infrared[5,6] spectroscopy. In these investigations, a monomeric model has frequently been adopted.[5,6] According to the X-ray analyses,[7-12] however, most copper-aminoacid complexes take complicated polymeric structures in the solid state. Since *trans*-bis(L-phenylalaninato)copper, Cu(DL-phe)$_2$, takes the polymeric structure shown in Fig. 1,[13] the monomeric model seems clearly inappropriate. In chapter IV, it has been revealed that polymeric *trans*- and *cis*-bis(D-alaninato)copper, Cu(D-ala)$_2$, show three and two appreciably sensitive to ^{63}Cu-^{65}Cu substitution, respectively. This chapter describes that the IR spectra of Cu(L-phe)$_2$ and an isomer of Cu(DL-phe)$_2$ are consistent with those of *trans*-Cu(D-ala)$_2$ and the IR spectrum of the other isomer of Cu(DL-phe)$_2$ is consistent with that of *cis*-Cu(D-ala)$_2$.

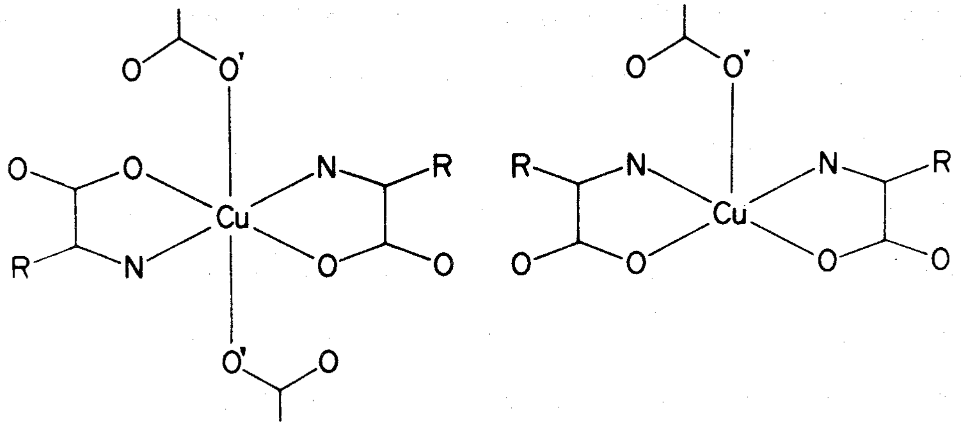
V-2 Experimental

V-2.1 Materials

Commercially available L- and DL-phenylalanines (Ishizu Seiyaku) were recrystallized several times from water. *N*-Deuterated L- and DL-phenylalanines were obtained from the purified L- and DL-phenylalanines by the usual exchange reaction with heavy water (Merck, AG., 99%). Cu(L-phe)$_2$ and two isomers of Cu(DL-phe)$_2$ were prepared from the purified L- and DL-phenylalanines according to the method of Laurie.15) A blue isomer (α-form), α-Cu(DL-phe)$_2$, prepared at room temperature was converted by heating on a boiling water bath into a blue-violet isomer (β-form), β-Cu(DL-phe)$_2$. For the preparation of *N*-deuterated complexes, Cu(L-phe-d_2)$_2$ and Cu(DL-phe-d_2)$_2$, anhydrous cupric acetate was reacted with the *N*-deuterated ligands in heavy water. The IR spectra of Cu(L-phe)$_2$, and α- and β-Cu(DL-phe)$_2$ in the region above 680 cm^{-1} coincided with those reported by Laurie.15) The complexes containing copper isotopes were obtained from isotopic cupric acetates which were prepared from ^{63}CuO and ^{65}CuO (Oak Ridge National Lab., USA) in the manner as described in chapter I. The yield was about 30 mg of the complexes from 7 mg of the isotopic CuO. The IR spectra of the complexes containing copper isotopes coincided with those of the complexes containing copper of natural abundance except for the copper isotope shifts. The isotopic purities were 99.89 % for ^{63}CuO and 99.70 % for ^{65}CuO.

V-2.2 Measurements

The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000 - 200 cm^{-1}). The measurements were made with solid samples in Nujol and hexachlorobutadiene (Merck, AG., Uvasol) mulls. The frequencies were calibrated by the standard absorptions of polystyrene, indene and water vapor. For measuring small shifts of band centers on ^{63}Cu and ^{65}Cu (^{63}Cu-^{65}Cu) substitution, the scale of the frequency was expanded ten times over the desired frequency region, and the measurements were repeated at least three times to check the reproducibility of the spectra.



*Trans*10,13)

*Cis*12)

Fig. 1 Polymeric *Trans* and *Cis* Structures for Cu(D-ala)$_2$ and Cu(L-phe)$_2$

The IR spectra in the region above 500 cm^{-1} of $Cu(L\text{-}phe)_2$, $Cu(DL\text{-}phe)_2$, and their *N*-deuterated analogues are shown in Fig. 2, and parts of the expanded spectra in Fig. 3.

V-3 Assignments and Discussion

The region between 4000 and 500 cm^{-1}.

No bands in the region above 500 cm^{-1} show an appreciable isotope shift on ^{63}Cu-^{65}Cu substitution except for some bands asterisked in Fig. 2 which show a small shift of less than 0.5 cm^{-1}. This small shift may be caused by a small contribution of the Cu-ligand stretching vibrations to the vibrations of phenylalaninates, and all the bands of $Cu(L\text{-}phe)_2$, and α- and β-$Cu(DL\text{-}phe)_2$ in this region were assigned to the vibrations of phenylalaninates. By referring to the frequency shifts on *N*-deuteration and the assignments of previous authors,[5,6] most of the bands were tentatively assigned to individual vibrations of phenylalaninates. By analogy with *trans*- and *cis*-$Cu(D\text{-}ala)_2$,[14] small differences of the IR spectra among three complexes were assumed to be caused by differences of the conformation of phenylalaninates. The IR spectra of the three complexes in this region give no clue to the structure of the coordination around the Cu atom.

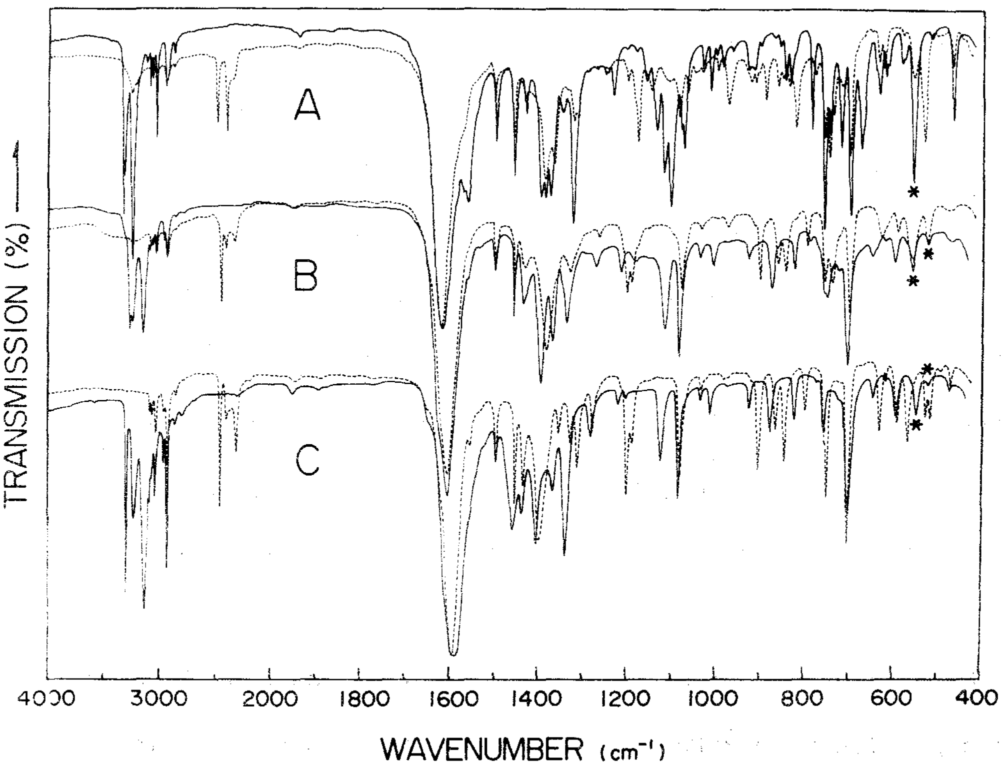


Fig. 2 IR Spectra of $Cu(L\text{-}phe)_2$, and α- and β-$Cu(DL\text{-}phe)_2$ in the Region above 450 cm^{-1},

A : $Cu(L\text{-}phe)_2$ (——) and $Cu(L\text{-}phe\text{-}d_2)_2$ (----);

B : α-$Cu(DL\text{-}phe)_2$ (——) and α-$Cu(DL\text{-}phe\text{-}d_2)_2$ (----);

C : β-$Cu(DL\text{-}phe)_2$ (——) and β-$Cu(DL\text{-}phe\text{-}d_2)_2$ (----).

The region between 500 and 200 cm^{-1}.

Bis(L-phenylalaninato)copper(II).

According to the X-ray analysis,13) the structure of $Cu(L\text{-}phe)_2$ resembles that of *trans*-bis(L-alaninato)copper(II).10) The copper coordination is a distorted octahedron including a *trans* square plane with two additional weak bonds (Cu-O', see Fig. 1). Since the copper atom occupies a symmetry site, C_1, in this environment, six Cu-ligand stretching vibrations are infrared-active. However, two Cu-O' bonds are so long that their stretching vibrations are probably in the region below 200 cm^{-1}.

Three band-centers of $Cu(L\text{-}phe)_2$ at 400, 380 and 339 cm^{-1} shift appreciably on ^{63}Cu-^{65}Cu substitution as shown in Fig. 3. These bands can undoubtedly be assigned to the vibrations including displacements of the copper atom. On *N*-deuteration, the 400 cm^{-1} band shifts to the lower frequency region by about 20 cm^{-1} and hides the 380 cm^{-1} band, whereas the 339 cm^{-1} band unshifts. Accordingly, the 400 cm^{-1} band was assigned to a Cu-N stretching vibration and the 380 and 339 cm^{-1} bands to the Cu-O stretching vibrations. It is consistent with the case of *trans*-$Cu(D\text{-}ala)_2$14) that three bands of $Cu(L\text{-}phe)_2$, two Cu-O and one Cu-N stretching bands, show an appreciable shift on ^{63}Cu-^{65}Cu substitution. The assignments based on the above discussion are summarized in Table I together with the observed frequencies, approximate intensities and isotope shifts on ^{63}Cu-^{65}Cu substitution.

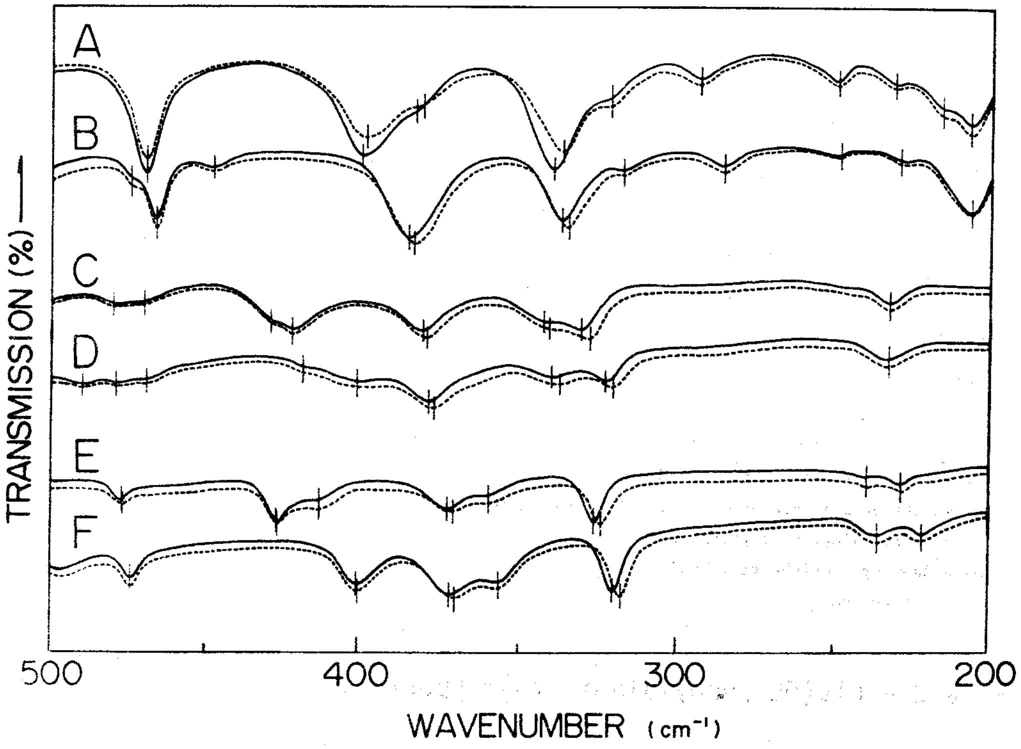


Fig. 3 Expanded IR Spectra of Cu(L-phe)$_2$, and α- and β-Cu(DL-phe)$_2$ in the Region between 500 and 200 cm^{-1},

A : ^{63}Cu(L-phe)$_2$ (——) and ^{65}Cu(L-phe)$_2$ (----);

B : ^{63}Cu(L-phe-d_2)$_2$ (——) and ^{65}Cu(L-phe-d_2)$_2$ (----);

C : α-^{63}Cu(DL-phe)$_2$ (——) and α-^{65}Cu(DL-phe)$_2$ (----);

D : α-^{63}Cu(DL-phe-d_2)$_2$ (——) and α-^{65}Cu(DL-phe-d_2)$_2$ (----);

E : β-^{63}Cu(DL-phe)$_2$ (——) and β-^{65}Cu(DL-phe)$_2$ (----);

F : β-^{63}Cu(DL-phe-d_2)$_2$ (——) and β-^{65}Cu(DL-phe-d_2)$_2$ (----).

Table I Observed Frequencies, Metal Isotope Shifts and Assignments for *trans*-Cu(L-phe)$_2$ and its *N*-Deuterated Analogues in the Region between 500 and 200 cm^{-1}

t-Cu(L-phe)$_2$				*t*-Cu(L-phe-d_2)$_2$		
$\nu^{a)}$	$\Delta\nu_m{}^{b)}$	Assign.$^{c)}$		$\nu^{a)}$	$\Delta\nu_m{}^{b)}$	Assign.$^{c)}$
		Herlinger *et al.*$^{5)}$	Present study			Present study
470 w	0	δskel	δskel	466 w	0	δskel
-$^{d)}$	-	-$^{e)}$	ν_sCu-NH$_2$	448 vw	0	ν_sCu-ND$_2$
400 w	1.2	ν_aCu-NH$_2$	ν_aCu-NH$_2$	385 w	1.5	ν_aCu-ND$_2$
380 sh	>1	δskel	ν_sCu-OOC	-$^{d)}$	-	ν_sCu-OOC
339 w	2.5	ν_aCu-OOC	ν_aCu-OOC	336 w	2.0	ν_aCu-OOC
320 sh	∿0	δskel	δskel	316 w	0	δskel
292 vw	0	δskel	δskel	284 vw	0	δskel
249 vw	0	δskel or δring.	δskel	247 vw	0	δskel
230 vw	0	-$^{e)}$	δskel	229 vw	0	δskel
215 sh	∿0	-$^{e)}$	δskel	-$^{d)}$	-	δskel
207 w	0	-$^{e)}$	δskel	206 w	0	δskel

a) w, weak; vw, very weak; sh, shoulder.

b) shifts of band center on ^{63}Cu-^{65}Cu substitution.

c) ν, stretching; δ, deformation.

d) hidden by a neighboring band.

e) not reported.

α- and β-Bis(DL-phenylalaninato)copper(II).

No X-ray analysis has yet been carried out for α- or β-Cu(DL-phe)$_2$ to date. Herlinger *et al.*$^{5)}$ concluded that the α- and β-forms were monomeric *trans*- and *cis*-conformations (C_i and C_s models), respectively, because the symmetric Cu-O and Cu-N stretching bands were missing in the IR spectrum of α-Cu(DL-phe)$_2$ as opposed to that of β-Cu(DL-phe)$_2$. However, by analogy with Cu(L-phe)$_2$$^{13)}$ and Cu(L-ala)$_2$$^{10)}$, it seems likely that the two isomers of Cu(DL-phe)$_2$ take polymeric structures, not monomeric structures.

Table II Observed Frequencies, Metal Isotope Shifts and Assignments for α-Cu(DL-phe)$_2$ and its *N*-Deuterated Analogues in the Region between 500 and 200 cm^{-1}

α-Cu(DL-phe)$_2$				α-Cu(DL-phe-d_2)$_2$		
$\nu$$^{a)}$	$\Delta\nu_m$$^{b)}$	Assign.$^{c)}$		$\nu$$^{a)}$	$\Delta\nu_m$$^{b)}$	Assign.$^{c)}$
		Herlinger *et al.*$^{e)}$	Present study			Present study
479 w	0	δskel	δskel	478 vw	0	δskel
469 sh	∿0	-$^{d)}$	δskel	468 sh	∿0	δskel
430 sh	∿0	δskel	ν_sCu-NH$_2$	415 sh	∿0	ν_sCu-ND$_2$
421 w	0	ν_aCu-NH$_2$	δskel	400 vw	0	δskel
380 w	1.0	δskel	ν_sCu-OOC	378 w	1.5	ν_sCu-OOC
340 sh	>1	δskel	ν_aCu-OOC	337 vw	2.0	ν_aCu-OOC
328 w	2.5	ν_aCu-OOC	ν_aCu-NH$_2$	320 w	2.2	ν_aCu-ND$_2$
230 vw	0	δskel	δskel	229 vw	0	δskel

a) w, weak; vw, very weak; sh, shoulder.
b) shifts of band center on ^{63}Cu-^{65}Cu substitution.
c) ν, stretching; δ, deformation.
d) not reported.
e) assuming a *trans*-monomeric model.$^{5)}$

Table III Observed Frequencies, Metal Isotope Shifts and Assignments for β-Cu(DL-phe)$_2$ and its *N*-Deuterated Analogues in the Region between 500 and 200 cm^{-1}

β-Cu(DL-phe)$_2$					β-Cu(DL-phe-d_2)$_2$		
$\nu$$^{a)}$	$\Delta\nu_m$$^{b)}$	Assign.$^{c)}$			$\nu$$^{a)}$	$\Delta\nu_m$$^{b)}$	Assign.$^{c)}$
		Herlinger *et al.*$^{f)}$	Inomata *et al.*$^{g)}$	Present study			Present study
474 vw	0.2	δskel	benzene ring	δskel	472 w	0	δskel
424 w	0.2	ν_aCu-NH$_2$	δskel	ν_sCu-NH$_2$	400 w	0.2	ν_sCu-ND$_2$
415 sh	∿0	ν_sCu-NH$_2$	-$^{e)}$	δskel	-$^{d)}$	-	δskel
370 vw	1.8	δskel	ν_aCu-NH$_2$	ν_aCu-OOC	369 w	1.5	ν_aCu-OOC
360 vw	0	ν_aCu-OOC	δskel	ν_sCu-OOC	357 w	0	ν_sCu-OOC
322 w	2.3	ν_sCu-OOC	δskel	ν_aCu-NH$_2$	316 w	2.2	ν_aCu-ND$_2$
236 vw	0	δskel	-$^{e)}$	δskel	232 vw	0	δskel
225 vw	0	δskel	-$^{e)}$	δskel	218 vw	0	δskel

a) w, weak; vw, very weak; sh, shoulder.
b) shifts of band center on ^{63}Cu-^{65}Cu substitution.
c) ν, stretching; δ, deformation.
d) hidden by a neighboring band.
e) not reported.
f) assuming a *cis*-monomeric model.$^{5)}$
g) assuming a *trans*-monomeric model.$^{6)}$

As shown in Fig. 3, the bands of α-$Cu(DL\text{-}phe)_2$ at 380, 340 and 328 cm^{-1} show appreciable isotope shift on ^{63}Cu-^{65}Cu substitution. Further, the 328 cm^{-1} band is replaced by a band at 320 cm^{-1} while the 380 and 340 cm^{-1} bands remain almost unshifted on *N*-deuteration. Accordingly, the 380 and 340 cm^{-1} bands were assigned to the Cu-O stretching vibrations and the 328 cm^{-1} band to a Cu-N stretching vibration. The number of copper isotope-sensitive bands for α-$Cu(DL\text{-}phe)_2$ is consistent with those for *trans*-polymeric $Cu(L\text{-}phe)_2$ and $Cu(D\text{-}ala)_2$.14)

For the β-form, two completely different assignments have been reported to date as shown in Table III. One was carried out by assuming a *trans* monomeric square model,6) whereas the other was based on a *cis* monomeric square model.5) Because of the ambiguity of the previous assignments, isotope labeling studies seemed essential.

The IR spectrum of β-$Cu(DL\text{-}phe)_2$ is similar to that of α-$Cu(DL\text{-}phe)_2$ as seen in Fig. 3. However, β-$Cu(DL\text{-}phe)_2$ shows only two appreciably copper isotope-sensitive bands at 370 and 322 cm^{-1} whereas α-$Cu(DL\text{-}phe)_2$ shows three. On *N*-deuteration, the 370 cm^{-1} band remains almost unshifted but the 322 cm^{-1} band shifts to a lower frequency region by about 10 cm^{-1}. By referring to these isotope shifts, the former can be assigned to a Cu-O stretching vibration and the latter to a Cu-N stretching vibration. It should be mentioned that the number of copper isotope-sensitive bands for β-Cu(DL-phe)$_2$ is in agreement with that of *cis*-polymeric Cu(D-ala)$_2$.14)

By referring to the frequency shifts on *N*-deuteration and the assignments for related complexes,14,16,17) the remaining bands of α- and β-Cu(DL-phe)$_2$ in the region between 500 and 200 cm^{-1} were tentatively assigned to skeletal deformation or Cu-ligand stretching vibrations involving little displacement of the Cu atom.

The assignments in this study are entirely different from those reported by previous authors5,6) as summarized in Tables II and III. This point suggests that the conventional methods used by the previous authors5,6) are frequently ineffective for assigning metal-ligand stretching vibrations and give ambiguous assignments for complicated metallo-aminoacids. In contrast, the shifts on ^{63}Cu-^{65}Cu substitution permit the unambiguous assignment of the vibrations including displacement of the copper atom.

The Cu-phenylalaninate stretching frequencies of α- and β-Cu(DL-phe)$_2$ are not very different from each other as can be seen in Tables II and III. As discussed above, the number of copper isotope-sensitive bands suggests that α- and β-Cu(DL-phe)$_2$ take the *trans*- and *cis*-polymeric structures, respectively. The Cu-N stretching frequencies of Cu(L-phe)$_2$ are higher by about 70 cm^{-1} than those of α- and β-Cu(DL-phe)$_2$, whereas the

Cu-O stretching frequencies are comparable with one another. This result is of interest, suggesting that the Cu-N binding forces are probably weakened by changing the ligand from L-phenylalanine to DL-phenylalanine.

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Chapter VI

Vibrational Spectra of Bis(L-serinato)-copper(II) and -zinc(II)

VI-1 Introduction

Recently, vibrational spectroscopy has been used increasingly for investigating the conformations of complicated vital molecules such as proteins and enzymes.1) The conformations of aminoacids on the surface of these vital molecules are of much interest in relation to their catalytic site.2) To provide a basis for such work, it is necessary to study the relationship between vibrational spectra and conformations of aminoacids. However, a given aminoacid which takes a particular conformation in the solid state3-5) often takes several conformations on complexation with metals.6-13) Metallo-aminoacids, which are models of the metallo-proteins and -enzymes, are suitable subjects for investigating the spectral differences caused by the conformational differences of aminoacids.

This chapter deals with bis(L-serinato)-copper(II) and -zinc(II) in order to clarify the difference of vibrational spectra between *gauche-gauche* and *anti-gauche* serinates (Fig. 1). The vibrational assignments have been carried out on the basis of the frequency shifts on metal isotope substitutions, which are very useful to assign the metal-ligand stretching vibrations of complicated metallo-aminoacids. In order to confirm the assignments, normal coordinate analysis for the Zn complex was carried out by using a complete molecular conformation and the inter- and intramolecular force fields.

VI-2 Experimental

VI-2.1 Materials

Commercially available L-serine (L-ser, Ishizu Seiyaku) was purified several times by recrystallization from a mixture of water and ethanol. *N*,*O*-Deuterated L-serine (L-ser-d_4) was obtained from the purified L-ser by the exchange reaction with heavy water (Merck, AG., 99%). Bis(L-serinato)copper(II), Cu(ser)$_2$, and bis(L-serinato)zinc(II), Zn(ser)$_2$, were prepared from the purified L-ser and the corresponding metal acetates. The IR spectra of these complexes were identical with those prepared from metal sulfate according to the method of van der Helm *et al.*[14,15] For the preparation of the *N*,*O*-deuterated complexes, Cu(ser-d_3)$_2$ and Zn(ser-d_3)$_2$, anhydrous cupric or zinc acetate was reacted with the L-ser-d_4 in heavy water. The precipitate was filtered, washed with a mixture of heavy water and ethanol-d_1 and dried over phosphorus pentoxide under reduced pressure. For the preparation of the complexes containing metal isotopes, ^{63}CuO, ^{65}CuO, ^{64}ZnO and ^{68}ZnO (Oak Ridge National Lab., USA) were converted into the corresponding cupric and zinc acetates by reaction with dilute acetic acid on a milligram scale. $^{63}Cu(ser)_2$, $^{65}Cu(ser)_2$, $^{64}Zn(ser)_2$ and $^{68}Zn(ser)_2$ and their *N*,*O*-deuterated analogues were prepared from the corresponding acetates in a similar way. The IR spectrum of each complex containing a metal isotope coincided with that of the complex containing the metal of natural abundance except for the metal isotope shifts. The isotopic purities were 99.89 % for ^{63}CuO, 99.70 % for ^{65}CuO, 99.85 % for ^{64}ZnO and 99.30 % for ^{68}ZnO.

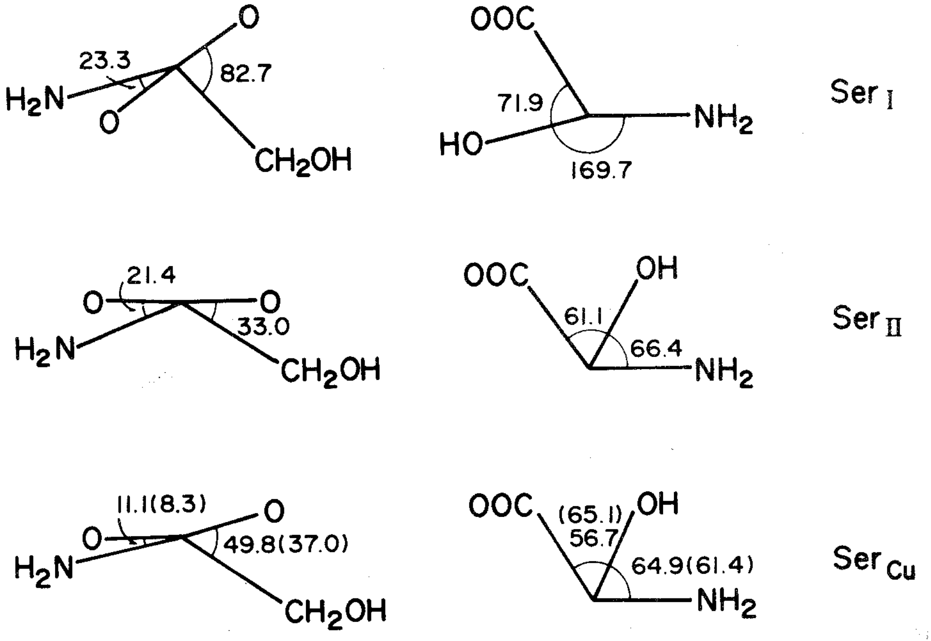

Fig. 1 Structures of L-serinate in $Cu(ser)_2$ and $Zn(ser)_2$

VI-2.2 Measurements

The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000 - 200 cm^{-1}). The measurements were made with solid samples in Nujol and hexachlorobutadiene (Merck, AG., Uvasol) mulls. The frequencies were calibrated by the standard absorptions of polystyrene, indene and water vapor. For measuring small shifts of band centers on ^{63}Cu-^{65}Cu and ^{64}Zn-^{68}Zn substitutions, the frequency scale was expanded ten times over the desired frequency region. The measurements were repeated at least three times to check the reproducibility of the spectra. The IR spectra of $Cu(ser)_2$ and $Zn(ser)_2$ in the region above 400 cm^{-1} are shown in Fig. 2 and parts of the expanded spectra in Fig. 3.

The Raman polarization measurement was carried out by using a single crystal of $Zn(ser)_2$ for which the directions of the cell axes, a, b and c' of the crystal were determined from an X-ray photograph. The Raman spectra excited by the 488.0 nm line of a Coherent 52G Ar^+ laser were recorded on a JEOL S-1 laser Raman spectrophotometer. The output power at the sample position was ca. 20 mW. The observed polarization spectra are shown in Fig. 4.

VI-3 Normal Coordinate Analysis

According to the X-ray analysis,14) $Zn(ser)_2$ takes a complicated polymeric structure chained by the bond between the zinc atom and a carboxylic oxygen from neighboring L-serinates. The optical active normal frequencies of $Zn(ser)_2$ were calculated by using the same program as described in chapter IV. By assuming the bond-lengths $r_{CH}=1.08$, $r_{NH}=1.02$ and $r_{OH}=1.00$ Å, the structure parameters were constructed on the basis of the X-ray analysis by van der Helm *et al.*14) A modified Urey-Bradley force field was used with a few valence type constants for the torsional and out-of-plane bending coordinates. The force constants related to L-serinates were initially transferred from DL-serine17) and the constants concerned with the copper atom from $Cu(DL\text{-}ser)_2$ reported by Inomata *et al.*18) The force constants asterisked in Table I were adjusted to improve the frequency fit. The force constants used in the final calculation are listed in Table I.

Initially, the calculation was carried out by using only the intramolecular forces. After slight adjustment of some force constants, the intermolecular forces were taken into account. By analogy with the previous treatments,14,19-22) the intermolecular potential was assumed to be the sum of the exp-6 type non-bonded atom-atom interaction terms, the Lippincott type hydrogen-bond stretching terms and the Coulomb interaction terms. In calculating the Coulomb interaction terms, the atomic charges of Zn(ser)$_2$ were estimated by CNDO/II calculation in which the zinc atom of Zn(ser)$_2$ was replaced by an Mg atom. The calculated frequencies in the final calculation are shown in Table II together with the observed frequencies. The calculated factor group splittings were less than 3 cm^{-1} in the region above 400 cm^{-1}. These splittings correspond well to the observed ones.

Table I Modified Urey-Bradley Type and Valence Type Force Constants

Modified Urey-Bradley type force constants$^{a)}$ (mdyn/Å)									
*K(C-O)	7.00$^{b)}$	H(OC'O)	0.06	*H(ZnNH)	0.10$^{b)}$	*F(OC'O)	4.00$^{b)}$	*F(ZnNH)	0.05$^{b)}$
K(C-C')	2.13	*H(OC'O)	0.35$^{b)}$	H(ZnNC)	0.05	F(OC'O)	0.70	F(ZnNC)	0.10
*K(C-H)	4.20$^{b)}$	H(C'CN)	0.65	*H(OC"C)	0.45$^{b)}$	F(C'CN)	0.60	F(OC"C)	0.761
K(C-N)	2.67	H(C'CC")	0.25	H(HC"H)	0.422	F(C'CC")	0.30	F(HC"H)	0.076
*K(N-H)	5.20$^{b)}$	H(C"CN)	0.22	H(OC"H)	0.119	F(C"CN)	0.60	F(OC"H)	0.637
K(C-C")	2.12	H(C'CH)	0.16	*H(C"OH)	0.25$^{b)}$	F(C'CH)	0.36	F(C"OH)	0.588
K(C"-O)	2.675	H(NCH)	0.25	H(ZnOC')	0.05	F(NCH)	0.54	*F(ZnOC')	0.10$^{b)}$
K(C"-H)	4.09	H(C"CH)	0.16	H(OZnN)$^{c)}$	0.05	F(C"CH)	0.40	*F(OZnN)$^{c)}$	0.05$^{b)}$
*K(O-H)	6.00$^{b)}$	H(CNH)	0.34	*H(OZnN)	0.05$^{b)}$	F(CNH)	0.50	*F(OZnN)	0.05$^{b)}$
*K(Zn-O)	0.20$^{b)}$	*H(HNH)	0.50$^{b)}$	*H(O'ZnO)	0.05$^{b)}$	F(HNH)	0.02	*F(O'ZnO)	0.05$^{b)}$
*K(Zn-N)	0.40$^{b)}$	H(CC"H)	0.245	*H(O'ZnN)	0.05$^{b)}$	F(CC"H)	0.502	*F(O'ZnN)	0.05$^{b)}$
*K(Zn-O')	0.35$^{b)}$	*κ(C')$^{d)}$	0.0$^{b)}$	*κ(C")$^{d)}$	0.0$^{b)}$	*κ(N)$^{d)}$	-0.05$^{b)}$		

Valence type force constants$^{a)}$ (mdyn·Å/rad^2)							
f(ωCO$_2$, ωCO$_2$)	1.92	f(τCC', τCC')	0.05	*f(τCN, τCN)	0.10$^{b)}$	f(τCC", τCC")	0.05
*f(τOH, τOH)	0.004$^{b)}$						

a) C, C' and C" denote the methine, the carboxylate and the methylene carbon atoms, respectively.

b) refined values.

c) force constant concerned in the chelate ring.

d) mdyn·Å.

VI-4 Assignments

The region above 450 cm^{-1}.

All the bands of Cu(ser)$_2$ in this region should be assigned to the vibrations of L-serinates, since no bands shift appreciably on ^{63}Cu-^{65}Cu substitution. According to the X-ray analysis,$^{15)}$ the two serinates in Cu(ser)$_2$ are similar to each other and take a *gauche-gauche* conformation as shown in Fig. 1. The assignments were given by referring to the frequency shifts on *N*,*O*-deuteration and the assignments for DL-serine$^{17)}$ and Cu(DL-ser)$_2$.$^{18)}$ They are summarized in Table II.

None of the bands of Zn(ser)$_2$ in this region show appreciable shifts on ^{64}Zn-^{68}Zn substitution and the bands are attributable to serinates. According to the X-ray analysis,$^{14)}$ the two serinates in Zn(ser)$_2$, ser$_{\mathrm{I}}$ and ser$_{\mathrm{II}}$, take the *anti-gauche* and the *gauche-gauche* conformations, respectively. By comparing the IR spectrum of Zn(ser)$_2$ with that of Cu(ser)$_2$, the vibrations due to ser$_{\mathrm{I}}$ can be distinguished from those due to ser$_{\mathrm{II}}$. In the region between 1800 and 800 cm^{-1}, the IR spectra of Cu(ser)$_2$ and Zn(ser)$_2$ are essentially similar to each other. However, some bands, for example the NH$_2$ wagging band around 1150 cm^{-1} and the skeletal stretching bands around 1040 cm^{-1}, split upon changing the Cu atom to the Zn atom. In order to clarify whether these splittings are caused by conformational difference between ser$_{\mathrm{I}}$ and ser$_{\mathrm{II}}$, the polarized

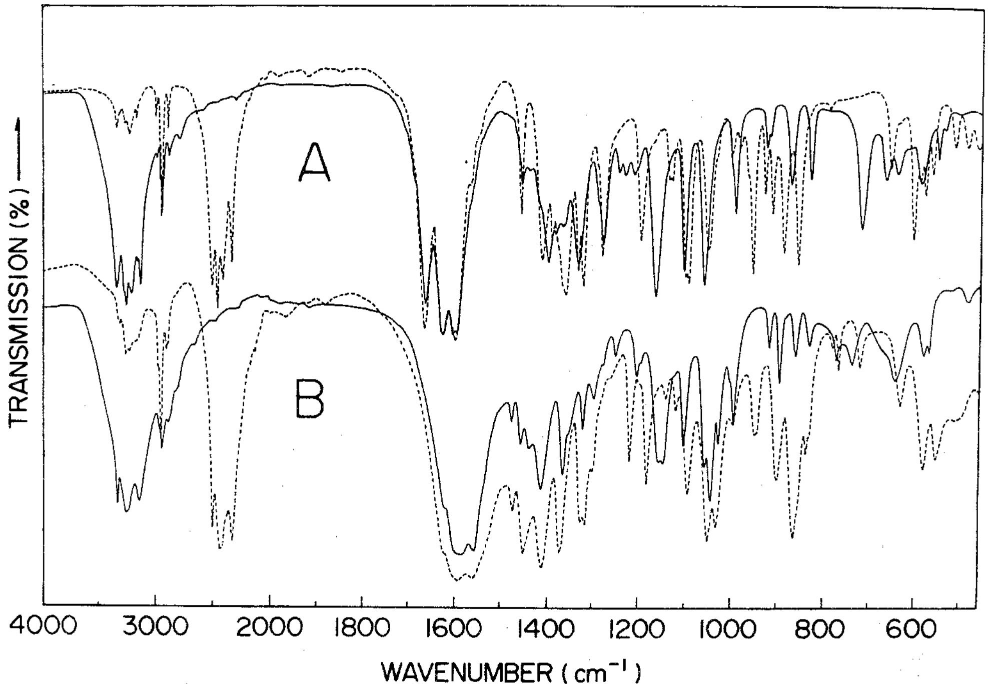

Fig. 2 IR Spectra of $Cu(ser)_2$, $Cu(ser\text{-}d_3)_2$, $Zn(ser)_2$ and $Zn(ser\text{-}d_3)_2$ in the Region above 450 cm^{-1}

A : $Cu(ser)_2$ (———) and $Cu(ser\text{-}d_3)_2$ (-----);

B : $Zn(ser)_2$ (———) and $Zn(ser\text{-}d_3)_2$ (-----).

Raman spectra of a single crystal of the Zn complex were analyzed. Since all the splittings are observed for the parallel and the perpendicular Raman spectra as shown in Fig. 4, these splittings should be due to conformational difference between ser_I and ser_{II}, and should not arise from the factor group splitting. In the infrared spectra between 800 and 720 cm^{-1}, $Cu(ser)_2$ shows no bands but replacement of the Cu atom

Table II Observed and Calculated Frequencies and Assignments for Cu(ser)$_2$, Zn(ser)$_2$ and their *N*,*O*-Deuterated Analogues in the Region between 4000 and 500 cm^{-1}

Cu(ser)$_2$	Zn(ser)$_2$		Assign.[c]	Cu(ser-d_3)$_2$	Zn(ser-d_3)$_2$		Assign.[c]
IR[a]	IR[a]	Calc.[b]		IR[a]	IR[a]	Calc.[b]	
3350 vs	3315 vs	3375	νOH(II)	*	2980 sh	2975	νCH(I)
*		3353	νOH(I)	2995 vw	2960 m	2965	νCH(II)
*	3240 vs	3194	ν_aNH$_2$(I)	2960 m 2940 m		2956	ν_aCH$_2$(II)
3255 vs 3205 vs	3220 sh	3188	ν_aNH$_2$(II)	*		2941	ν_aCH$_2$(I)
*	3125 vs	3139	ν_sNH$_2$(I)	2880 w	2910 w	2927	ν_sCH$_2$(II)
3125 vs		3133	ν_sNH$_2$(II)	*	2890 sh	2909	ν_sCH$_2$(I)
*	2965 sh	2975	νCH(I)	2490 vs	2500 vs	2451	νOD(II)
2980 vw		2965	νCH(II)	*		2436	νOD(I)
2935 m	2930 m	2956	ν_aCH$_2$(II)	*	2435 vs	2351	ν_aND$_2$(I)
*		2941	ν_aCH$_2$(I)	2445 vs 2440 vs	2430 sh	2347	ν_aND$_2$(II)
2875 vw	2875 sh	2927	ν_sCH$_2$(II)	*	2390 sh	2271	ν_sND$_2$(I)
*		2909	ν_sCH$_2$(I)	2320 vs	2335 vs	2267	ν_sND$_2$(II)
1660 vs	1630 sh		combination- or overtone	1660 vs	1630 sh		combination- or overtone
1626 vs 1600 vs	1590 vs	1616	ν_aCO$_2$(II)	1624 vs 1597 vs	1592 vs	1615	ν_aCO$_2$(II)
*	1558 vs	1604	ν_aCO$_2$(I)	*	1558 vs	1604	ν_aCO$_2$(I)
	1530[d] w	1536	βNH$_2$(II)	*	1472 m	1490	βCH$_2$(I)
*		1532	βNH$_2$(I)	1452 m	1450 m	1465	βCH$_2$(II)
*	1472 w	1490	βCH$_2$(I)	*	1409 m	1416	ν_sCO$_2$(I)
1452 m	1452 w	1465	βCH$_2$(II)	1410 m		1412	ν_sCO$_2$(II)
1438 vw	1437 w		combination- or overtone	1353 s	1369 m	1341	δCH'(II)
*	1411 m	1415	ν_sCO$_2$(I)	*	1324 m	1326	δCH'(I)
1396 m		1412	ν_sCO$_2$(II)	1331 m 1315 m	1313 m	1296	ωCH$_2$(II)
1364 vw	1363 m	1354	δCH'(II)	*	1297 sh	1287	ωCH$_2$(I)
*	1351 sh	1336	tNH$_2$(I)	*	1275 sh	1260	tCH$_2$(I)
*		1330	δCH'(I)	1275 m	1256 sh	1242	tCH$_2$(II)
1328 m	1319 m	1312	tNH$_2$(II)	1191 m	1217 m	1199	δCH(II)
*	1295 w	1294	ωCH$_2$(I)	*	1180 m	1187	δCH(I)
1285 sh 1275 m	1270 w	1274	ωCH$_2$(II)	*	1139 w	1147	βND$_2$(I)
*	1245 w	1243	tCH$_2$(I)	1130 m 1122 m	1117 w	1128	βND$_2$(II)
1240 w		1238	tCH$_2$(II)	1093 m 1085 m	1090 m	1084	νskel(II)
*	1199 m	1216	δOH(I)	*		1087	νskel(I)
1162 s	1190 sh	1193	δOH(II)	*	1048 m	1067	tND$_2$(I)
*	1152 m	1156	ωNH$_2$(I)	1045 m		1058	νskel(II)
1228 w 1208 w	1142 m	1148	ωNH$_2$(II)			1037	tND$_2$(II)

Table II (continued)

1100 m	1120 sh	1117	δCH(II)	*	1029 m	1019	νskel(I)
	1098 m	1101	νskel(II)	*	994 w	987	νskel(I)
*		1098	δCH(I)	945 m	947 m	963	νskel(II)
*	1052 m	1091	νskel(I)	*		957	δOD(I)
1056 m	1039 s	1043	νskel(II)	993 w 975 w	943 sh	949	δOD(II)
*	1023 m	1029	νskel(I)	*	898 m	883	νskel(I)
*	1000 sh	997	νskel(I)	919 m 901 m		903	νskel(II)
995 sh 987 m	994 m	995	νskel(II)	875 m	862 m	872	ωND$_2$(II)
*		979	νskel(I)	*	855 sh	856	ωND$_2$(I)
920 m 912 sh	912 m	932	νskel(II)	*	844 w	805	ρCH$_2$(I)
*	888 m	878	ρCH$_2$(I)	846 m	827 sh	795	ρCH$_2$(II)
866 m	857 m	852	ρCH$_2$(II)	778 vw	777 w	760	ωCO$_2$(II)
823 m	822 m	818	ωCO$_2$(II)	*	762 m	750	ωCO$_2$(I)
*	764 m	754	ωCO$_2$(I)	*	714 m	726	βCO$_2$(I)
*	728 m	745	βCO$_2$(I)	643 m	627 m	640	βCO$_2$(II)
710 m	654 sh	673	ρNH$_2$(II)	593 m	575 m	604	δskel(II)
656 m	637 m	662	βCO$_2$(II)	*	549 m	550	ρCO$_2$(I)
*	654 sh	654	ρNH$_2$(I)	552 m	545 sh	547	ρCO$_2$(II)
631 m	572 m	601	δskel(II)	*	510 w	526	ρND$_2$(I)
*	556 m	566	ρCO$_2$(I)	506 m	490 w	479	ρND$_2$(II)
500 vw	510 vw	526	ρCO$_2$(II)	565 m 552 m	449 w	474	δskel(II)
581 m	478 w	478	δskel(II)	*	432 w	426	δskel(I)
530 vw 545 w		449	δskel(II)	475 m 452 w	415 w	396	δskel(II)
*	425 w	424	δskel(I)	336 w	320 w	324	δskel
344 w	334 w	357	δskel		310 vw	308	δskel
	315 vw	329	δskel	302 w	270 w	292	δskel or νMe-ligand
308 w	280 w	299	δskel or νMe-ligand	373 w	285 w	270	νMe-ligand
377 w	295 w	276	νMe-ligand	267 w	–e)	249	δskel
275 w	250d) w	255	δskel	252 vw	–e)	238	δskel or νMe-ligand
255 w		251	δskel or νMe-ligand	323 w	225 w	206	νMe-ligand
327 m	230 w	230	νMe-ligand	245 sh	–e)	199	δskel
223 w	198d) w	207	δskel	214 vw	–e)	190	δskel

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; *, not expected.

b) species A.

c) ν, stretching; β, bending; δ, deformation; *t*, twisting; ω, wagging; ρ, rocking.

d) Raman frequencies.

e) not observed.

with a Zn atom gives rise to two bands at 764 and 728 cm^{-1} assignable to the COO wagging and the COO bending vibrations, respectively, of ser_I by referring to the initially calculated frequencies and the shifts on *N*,*O*-deuteration. On a similar basis, the bands of $Zn(ser)_2$ at 822 and 637 cm^{-1} are assigned to the COO wagging and bending vibrations, respectively, of ser_{II}. As expected from the conformational analogy, the corresponding bands of $Cu(ser)_2$ are observed at 823 and 656 cm^{-1}. The maximum frequency difference between ser_I and ser_{II} amounts to 91 cm^{-1} for the COO bending bands. The assignments of $Zn(ser)_2$ discussed above are summarized in Table II together with the observed and the calculated frequencies.

The region between 450 and 200 cm^{-1}.

According to the X-ray analyses,[14,15] the coordination structure of $Zn(ser)_2$ is approximately square-pyramidal while that of $Cu(ser)_2$ is intermediate between square-pyramidal and trigonal-bipyramidal. Since the central metal atom occupies a symmetry site, C_1, in these environments, five metal-ligand stretching vibrations are infrared-active. However, one of the Cu-OOC bonds is so long (2.36 Å) that its stretching vibration may not be observed in the region above 200 cm^{-1}.

For $Cu(ser)_2$, seven bands were observed at 377, 344, 327, 308, 275, 255 and 223 cm^{-1} as shown in Fig. 3. Previously, Canham *et al.*[23)] assigned the 377 and 327 cm^{-1} bands to the Cu-N and the Cu-O stretching vibrations, respectively. On ^{63}Cu-^{65}Cu substitution, all the bands in this region except the 223 cm^{-1} band show isotope shifts larger than 0.7 cm^{-1} as shown in Fig. 3. Since the 377 and 327 cm^{-1} bands show relatively large isotope shifts by about 2 cm^{-1} on ^{63}Cu-^{65}Cu substitution and shift to the lower frequency region by about 4 cm^{-1} on *N*,*O*-deuteration, it is reasonable to assign these bands to complicated vibrations caused by coupling between the Cu-O and the Cu-N stretching vibrations. By referring to the assignments of bis(alaninato)copper(II),[16)] the 255 and the 308 cm^{-1} bands were assigned to the symmetrical Cu-ligand stretching vibrations. By analogy with L-ser,[24)] the three bands at 344, 275 and 223 cm^{-1} were assigned to the skeletal deformation vibrations. Small isotope shifts of some of them on ^{63}Cu-^{65}Cu substitution may be caused by a small contribution of the Cu-ligand stretching vibrations.

$Zn(ser)_2$ shows six bands at 425, 334, 320, 295, 280 and 230 cm^{-1} in the region between 450 and 200 cm^{-1}. As shown in Fig. 2, only the bands at 295 and 230 cm^{-1} show appreciable isotope shifts larger than 2 cm^{-1} on ^{64}Zn-^{68}Zn substitution while the six bands of the Cu complex show similar shifts on

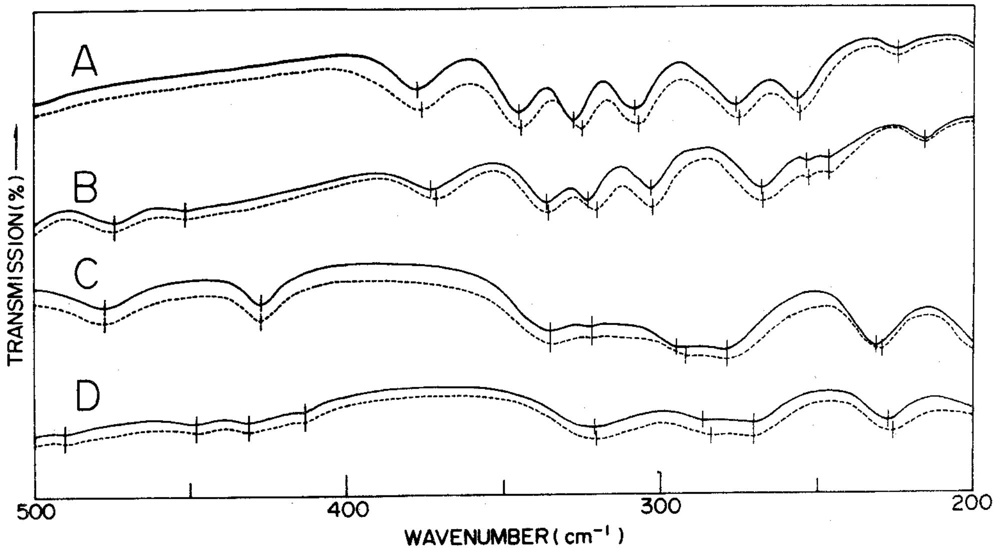

Fig. 3 Expanded IR Spectra of $Cu(ser)_2$, $Cu(ser\text{-}d_3)_2$, $Zn(ser)_2$ and $Zn(ser\text{-}d_3)_2$ in the Region between 500 and 200 cm^{-1}

A : $^{63}Cu(ser)_2$ (———) and $^{65}Cu(ser)_2$ (-----);

B : $^{63}Cu(ser\text{-}d_3)_2$ (———) and $^{65}Cu(ser\text{-}d_3)_2$ (-----);

C : $^{64}Zn(ser)_2$ (———) and $^{68}Zn(ser)_2$ (-----);

D : $^{64}Zn(ser\text{-}d_3)_2$ (———) and $^{68}Zn(ser\text{-}d_3)_2$ (-----).

^{63}Cu-^{65}Cu substitution. By referring to the frequency shifts on *N*,*O*-deuteration, the bands at 295 and 230 cm^{-1} were assigned to the Zn-N stretching vibration and the Zn-O asymmetrical stretching vibration, respectively. The remaining bands were assigned to the skeletal deformation vibrations by referring to the frequency shift on *N*,*O*-deuteration and the initial calculation. The conformational difference between ser_I and

Table III Observed Frequencies, Metal Isotope Shifts and Assignments for $Cu(ser)_2$ and $Cu(ser\text{-}d_3)_2$ in the Region between 450 and 200 cm^{-1}

$Cu(ser)_2$ [a)]	$\Delta\nu_m$ [b)]	$Cu(ser\text{-}d_3)_2$ [a)]	$\Delta\nu_m$ [b)]	Assignments[c)]
377 w	1.7	373 w	1.7	ν_aCu-OOC + ν_aCu-$NH_2(ND_2)$
344 w	0.7	336 w	0.6	δskel
327 m	2.6	323 w	2.9	ν_aCu-OOC + ν_aCu-$NH_2(ND_2)$
308 w	1.2	302 w	0.5	ν_sCu-OOC + ν_sCu-$NH_2(ND_2)$
275 w	1.0	267 w	0.4	δskel
255 w	0.7	252 vw	0.6	ν_sCu-OOC + ν_sCu-$NH_2(ND_2)$
-[d)]	-	245 sh	∿0	δskel
223 vw	0	214 w	0	δskel

a) m, medium; w, weak; sh, shoulder.

b) shifts of band center on ^{63}Cu-^{65}Cu substitution.

c) ν, stretching; δ, deformation.

d) hidden by a neighboring band.

Table IV Observed and Calculated Frequencies, Metal Isotope Shifts and Assignments for $Zn(ser)_2$ and $Zn(ser\text{-}d_3)_2$ in the Region between 450 and 200 cm^{-1}

$Zn(ser)_2$				$Zn(ser\text{-}d_3)_2$				
Obs.[a)]	Calc.	$\Delta\nu_m$ [b)]		Obs.[a)]	Calc.	$\Delta\nu_m$ [b)]		Assignments[c)]
		Obs.	Calc			Obs.	Calc.	
425 w	424	0	0.0	415 w	396	0	0.0	δskel
334 w	357	0	0.0	320 w	324	0.4	0.1	δskel
315 vw	329	0	0.2	310 vw	308	0	0.2	δskel
295 w	276	∿3	2.9	285 w	270	3	3.4	νZn-$NH_2(ND_2)$
280 w	299	0	0.6	270 w	292	0	0.5	δskel
250[d)] w	255 251	-	0.8 1.3	-[e)]	249 238	-	0.9 1.7	δskel
230 w	230	2.1	1.1	225 w	206	1.6	2.4	νZn-OOC
198[d)] w	207	-	0.0	-[e)]	199	-	0.2	δskel

a) w, weak; sh, shoulder.

b) shifts of band center on ^{64}Zn-^{68}Zn substitution.

c) ν, stretching; δ, deformation.

d) Raman frequencies.

e) not reported.

ser_{II} is indistinct with respect to their skeletal deformation vibrations because of the complicated coupling with the metal-ligand stretching vibrations. The assignments are summarized in Tables III and IV together with the frequencies and the isotope shifts.

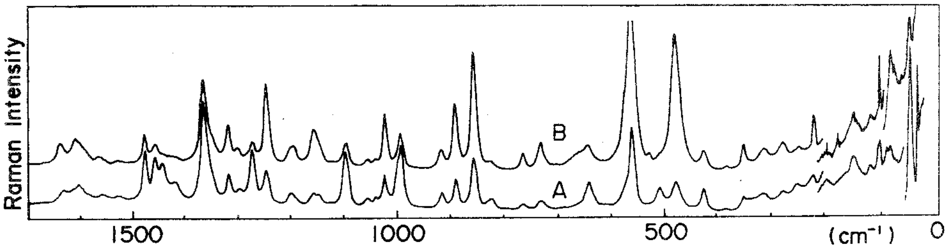

Fig. 4 Polarized Raman Spectra of $Zn(ser)_2$ Single Crystal
A : a(ba)b; B : a(bc')b.

VI-5 Discussion

As shown in Table IV, the final calculation reproduced well the observed isotope shifts on ^{64}Zn-^{68}Zn substitution supporting the assignments in this work. In this calculation, the intermolecular force was found to play an essential role in reproducing the observed shifts. The calculated L matrices reveal that the Zn-O stretching vibrations couple with most of the skeletal deformation vibrations. This coupling may be one of the reasons why the skeletal deformation frequencies of ser_{Cu} are very different from those of ser_{II}.

As can be seen in Table II, the agreement between the calculated and the observed frequencies of $Zn(ser)_2$ and $Zn(ser\text{-}d_3)_2$ is satisfactory in spite of the crude approximation of using the same force constants for ser_I and ser_{II}. The agreement indicates that the frequency differences between ser_I and ser_{II} are due mainly to the conformational difference, and the change of the force constants seems to be rather unimportant. The frequency differences between ser_I and ser_{II} are summarized in Table V. The calculated differences follow well the observed trend, including large differences in the COO deformation and the skeletal stretching frequencies.

Table V Observed and Calculated Frequency Differences between ser_I and ser_{II} in the Region between 1700 and 500 cm^{-1}

$Zn(ser)_2$		$Zn(ser\text{-}d_3)_2$		Bands[b)
Obs.[a)	Calc.[a)	Obs.[a)	Calc.[a)	
-32	-12	-34	-11	ν_aCO_2
0[c)	-4	22	19	$\beta NH_2(ND_2)$
20	25	22	25	βCH_2
0	3	0	4	ν_sCO_2
-12	-24	-45	-15	$\delta CH'$
32	24	0	24	$t NH_2(ND_2)$
25	20	-16	-9	ωCH_2
0	5	19	18	$t CH_2$
9	23	4	8	$\delta OH(OD)$
10	8	-7	-16	$\omega NH_2(ND_2)$
-22	-19	-37	-12	δCH
-46	-10	0	3	νskel
-16	-14	-19	-39	νskel
6	2	47	24	νskel
82	47	0	-20	νskel
31	26	17	10	ρCH_2
-58	-64	-15	-10	ωCO_2
91	83	87	86	βCO_2
0	-19	0	47	$\rho NH_2(ND_2)$
46	40	4	3	ρCO_2

a) Frequency difference = ν(*anti-gauche*) - ν(*gauche-gauche*)

b) ν, stretching; δ, deformation; t, twisting; ω, wagging; ρ, rocking; β, bending.

c) Raman frequency difference.

VI-6 References

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Chapter VII

Conclusions

[I] The infrared spectrum of bis(L-asparaginato)copper(II) has been investigated by means of metal isotope technique. By referring to the isotope shifts on ^{63}Cu-^{65}Cu substitution, two bands at 359 and 318 cm^{-1} have been assigned to the Cu-ligand stretching vibrations. It has been revealed that the metal isotope technique is very useful for assigning the metal-ligand stretching vibrations, for which conventional methods cannot give any unique assignments.

[II] The infrared spectrum of bis(L-asparaginato)zinc(II) has been investigated by means of metal isotope technique. By referring to the isotope shifts on ^{64}Zn-^{68}Zn substitution, three bands at 301, 265 and 244 cm^{-1} have been assigned to the Zn-ligand stretching vibrations. This result reveals that the binding force of the Zn-O bond of zinc-aminoacids is much stronger than considered previously.

[III] The infrared spectra of copper(II)- and zinc(II)-L-glutamate dihydrates and their deuterated complexes have been investigated by means of metal isotope technique. Appreciable shifts have been observed for bands at 404, 352 and 279 cm^{-1}

of the Cu complex and bands at 229, 245 and 227 cm^{-1} of the Zn complex on metal indicate that the Cu-OOC stretching vibration responsible for the band around 280 cm^{-1} is localized whereas the Zn-OOC stretching vibrations couple with Zn-NH_2 and/or Zn-OH_2 stretching vibrations.

[IV] The infrared spectra of *trans*- and *cis*-bis(D-alaninato)-copper(II) have been investigated by means of metal isotope technique. It has been revealed that the *trans*-isomer shows three copper isotope sensitive bands, while the *cis*-isomer shows two. However, the Cu-ligand stretching frequencies of the two conformers are not much different from each other. The normal coordinate analysis by using a complete molecular conformation and the inter- and intramolecular force fields indicates that the intramolecular force fields of the *trans* and the *cis* isomers differ only slightly from each other.

[V] The infrared spectra of two isomers of Cu(DL-phenyl-alaninate)$_2$, the structures of which are unknown to date, have been dealt with by means of metal isotope technique. It has been revealed that the blue isomer of Cu(DL-phe)$_2$ shows three copper isotope sensitive bands, while the blue-violet isomer of Cu(DL-phe)$_2$ shows two. By analogy with *trans*- and *cis*-Cu(D-alaninate)$_2$, this result suggests that the blue and the blue-violet isomers take the polymeric *trans* and *cis* structures, respectively.

[VI] Metal isotope technique is also effective for assigning the metal-ligand stretching vibrations of bis(L-serinato)-copper(II) and -zinc(II). By comparing the infrared spectrum of the Zn complex with that of the Cu complex, it has been revealed that the structural difference between the *anti-gauche* and the *gauche-gauche* serinates in the Zn complex is reflected clearly in the COO deformation and the skeletal stretching vibrations. The calculated frequencies and frequency differences between the two serinates agree well with the observed ones. This agreement reveals that the frequency differences are due mainly to the conformational difference, and the change of the force constants is unimportant.