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Metal Isotope Effects on the Vibrational Spectra of Polymeric Metal Complexes. II.[1] Infrared Spectra of Copper and Zinc Glutamate Dihydrates[2]

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The infrared spectra of $[Cu(glutamate)\cdot(H_2O)]_n\cdot(H_2O)_n$, $[Zn(glutamate)\cdot(H_2O)]_n\cdot(H_2O)_n$ and their isotopic complexes containing metal and hydrogen isotopes have been measured in the region between 4000 and 200 cm^{-1}. The isotope shifts on ^{63}Cu and ^{65}Cu substitution have been observed for bands at 404, 352 and 279 cm^{-1} of the Cu complex. Bands at 300, 245 and 227 cm^{-1} of the Zn complex are apparently sensitive to ^{64}Zn and ^{68}Zn substitution. The frequency shifts on *N*,*O*-deuteration indicated that a Cu-OOC stretching vibration is localized for the Cu complex whereas Zn-OOC stretching vibrations couple with $Zn-NH_2$ and/or $Zn-OH_2$ stretching vibrations.

Keywords——infrared spectra; metal complex; metal isotope effect; ^{63}Cu and ^{65}Cu substitution; ^{64}Zn and ^{68}Zn substitution; copper glutamate dihydrate; zinc glutamate dihydrate; deuteration; amino acid; glutamic acid

Complexes containing glutamic acid have centered much interest because of their biological properties,[3-5] and have been investigated by various methods.[6-18] However, it seems to be rather difficult to analyze the infrared (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[8-12] and electron spin resonance (ESR) spectra.[13-18] On the other hand, it has previously been shown for a complicated polymeric complex, [bis(L-asparaginato)copper(II)]$_n$, that the metal isotope technique is very useful to assign the vibrations including displacement of the metal.[19]

In the present work, 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.

Experimental Results

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 dihydrate (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.*[8,9] 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 the ^{63}CuO, 99.70% for the ^{65}CuO, 99.85% for the ^{64}ZnO and 99.30% for the ^{68}ZnO.

Measurements——The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000—200 cm^{-1}). The measurements were made on solid samples in Nujol or hexachlorobutadiene (Merck, AG, Uvasol) mull. 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 analogs are shown in Fig. 1 and parts of the expanded spectra are shown in Fig. 2.

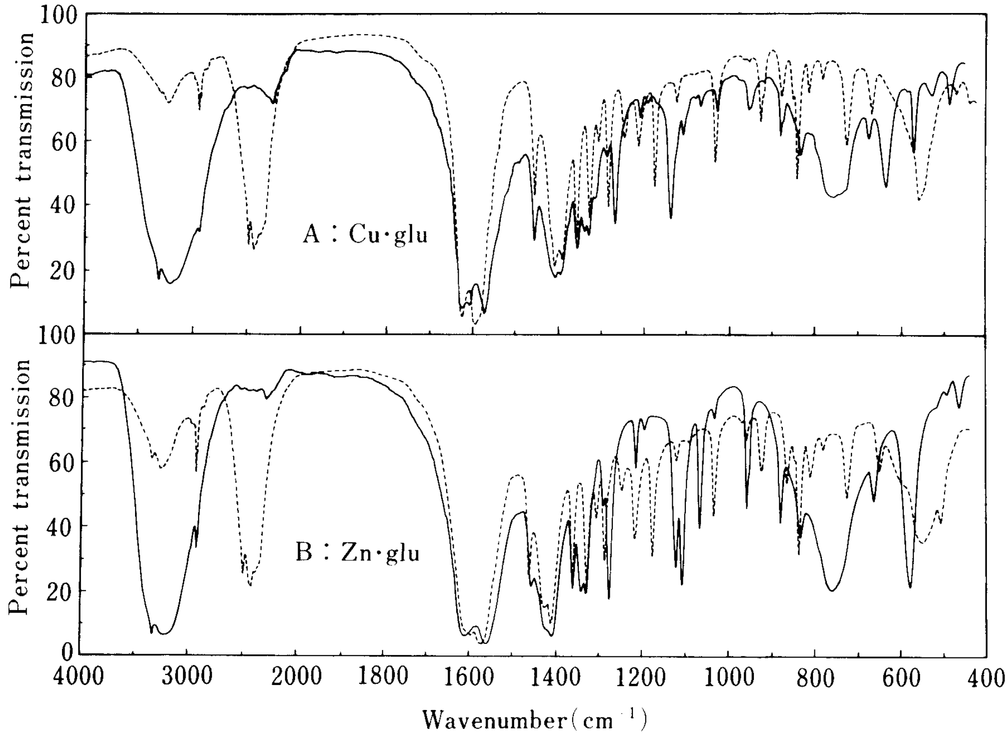

Fig. 1. IR Spectra of Cu·glu and Zn·glu in the Region above 400 cm^{-1}

A: Cu·glu (——) and Cu·glu-d_6 (----); B: Zn·glu (——) and Zn·glu-d_6 (----).

Vibrational Assignments and Discussion

In 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,[8,9] 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 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 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.[20–23] 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.

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	tCH_2
1192 w	1174 m	1188 w	1176 m	tCH_2
1138 m	881 m	1121 m	863 m	$\omega NH_2(ND_2)$
1109 w	843 m	1107 m	835 m	$tNH_2(ND_2)$
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 the Region between 500 and 200 cm^{-1}

According to the X-ray analyses,[8,9] 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.

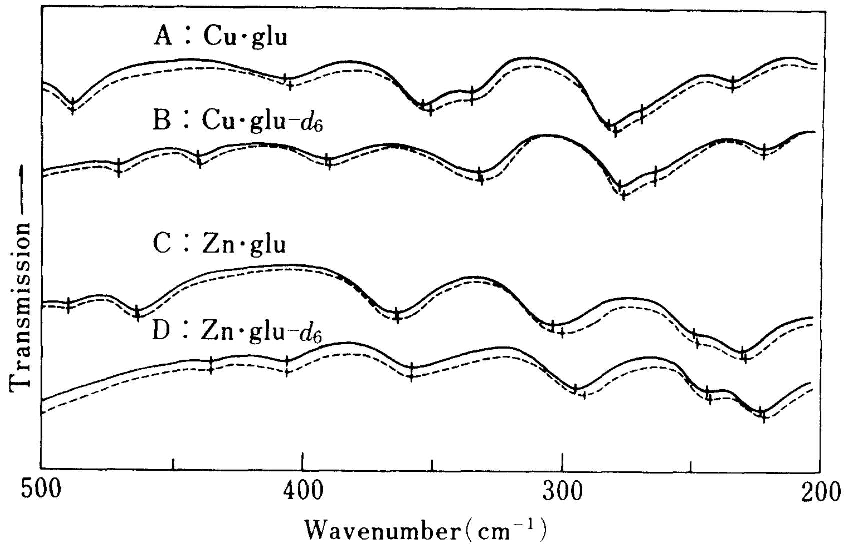

Fig. 2. IR Spectra of Cu·glu and Zn·glu in the Region between 500 and 200 cm^{-1}

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 (-----).

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 the Cu–ligand stretching vibrations. The reason is that the skeletal deformation frequencies should be different from those of Na·glu bacause 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 modes of these bands include a small displacement of active hydrogen atoms. Accordingly, we assigned these bands 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

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.

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 300, 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, we assigned these three bands of Zn·glu 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.

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.

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.[8,9] 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*-[25] and *cis*-bisglycinatocopper complexes[25] and is comparable with that of polymeric $[Cu(asparaginate)_2]_n$.[19] This may indicate that polymerization through bridges of ligand molecules plays a role in decreasing the Cu–OOC stretching frequency, as pointed out in the previous paper.[19]

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,[26) 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.[27,28) 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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