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Metal Isotope Effects on the Vibrational Spectra of Polymeric Metal Complexes. III.[1] Infrared Spectra of [Bis(L-asparaginato)zinc(II)]$_n$

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The infrared spectra of [bis(L-asparaginato)zinc(II)]$_n$ and its isotopic complexes containing ^{64}Zn, ^{68}Zn and deuterium have been measured in the region between 4000 and 200 cm^{-1}. By referring to the isotope frequency shifts, three bands at 301, 265 and 244 cm^{-1} have been assigned to Zn-ligand stretching vibrations caused from coupling among Zn–O and Zn–N stretching vibrations. The frequency range of the Zn–O stretching vibrations suggests that the Zn–O binding force of zinc-amino acids is probably larger than has been considered.

Keywords——infrared spectra; polymeric metal complex; asparagine; amino acid; isotope effect; ^{64}Zn and ^{68}Zn substitution; Zn-ligand stretching vibration; deuteration; bis(L-asparaginato)zinc

Since metal-amino acid complexes are fundamental compounds of metallo-proteins and -enzymes, it is of interest to elucidate the metal-ligand stretching frequencies of amino acid complexes. It has recently been shown that the metal isotope technique is very useful to identify the infrared (IR) absorption bands due to the metal-ligand stretching vibrations of polymeric metal-aminoacid complexes,[2,3] such as [bis(L-asparaginato)copper(II)]$_n$, which are also of interest because of their biological activities in cancer chemotherapy, *etc.*[4-6] In the present study, the metal isotope technique, ^{64}Zn and ^{68}Zn substitution, has been applied to analyze 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 amino acids.

Experimental Results

Materials——Purified L-asparagine monohydrate and *N*,*N′*-deuterated L-asparagine monohydrate (aspn·H_2O and aspn-d_5·D_2O) were obtained by the same manner as described previously.[2] [Bis(L-asparaginato)zinc(II)]$_n$, [Zn(aspn)$_2$]$_n$, was prepared from the purified aspn·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 Stephans *et al.*[7] For the preparation of *N*,*N′*-deuterated complex, [Zn(aspn-d_4)$_2$]$_n$, anhydrous zinc acetate was reacted with aspn-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 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 aspn·H_2O or aspn-d_5·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 the ^{64}ZnO and 99.00% 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 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 $[Zn(aspn)_2]_n$ and $[Zn(aspn\text{-}d_4)_2]_n$ are shown in Fig. 1, and parts of the expanded spectra in Fig. 2.

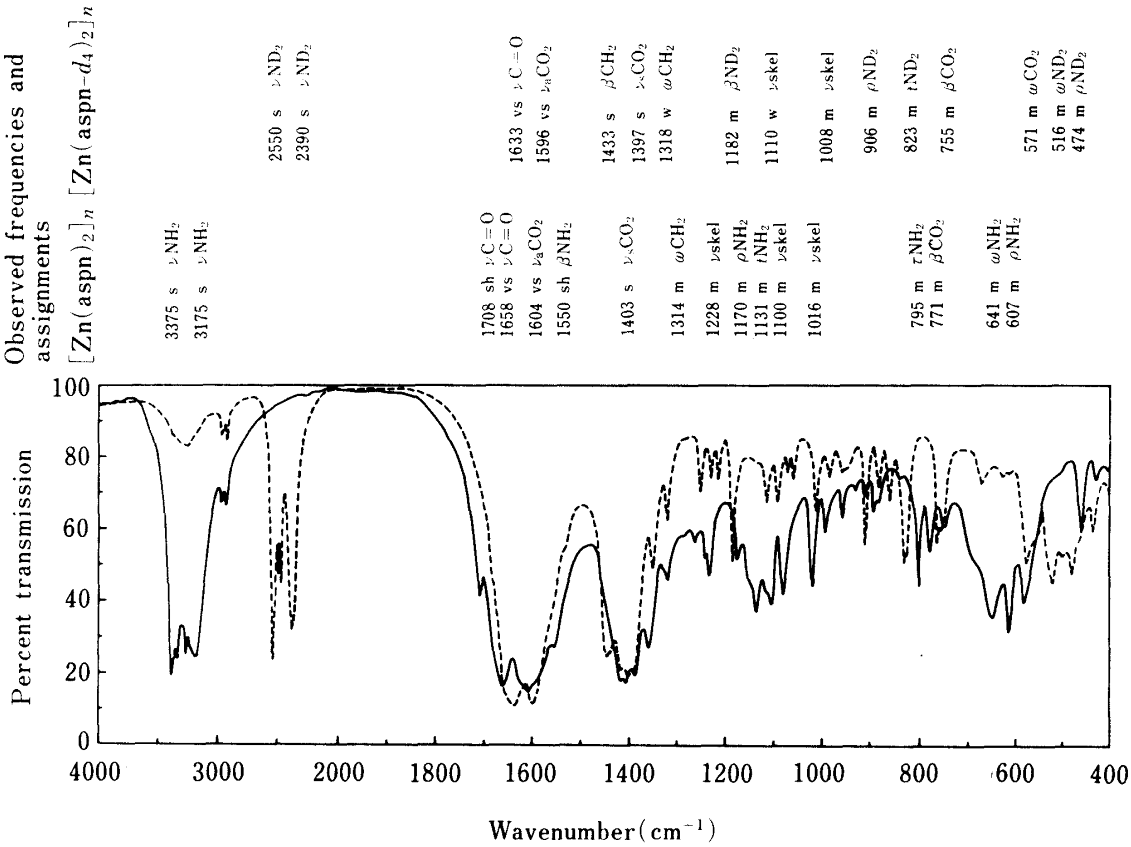

Fig. 1. IR Spectra and Band Assignments of $[Zn(aspn)_2]_n$ and $[Zn(aspn\text{-}d_4)_2]_n$ in the Region above 400 cm^{-1}

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

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.

Vibrational Assignments and Discussion

In 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 $[Zn(aspn)_2]_n$ and $[Zn(aspn\text{-}d_4)_2]_n$ were essentially similar to those of the corresponding Cu complexes,[2] 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, we assigned all the bands in this region 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.

In the Region between 400 and 200 cm^{-1}

According to the X-ray analysis,[7] 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}, we can expect two Zn–O and two Zn–N stretching vibrations in this region.

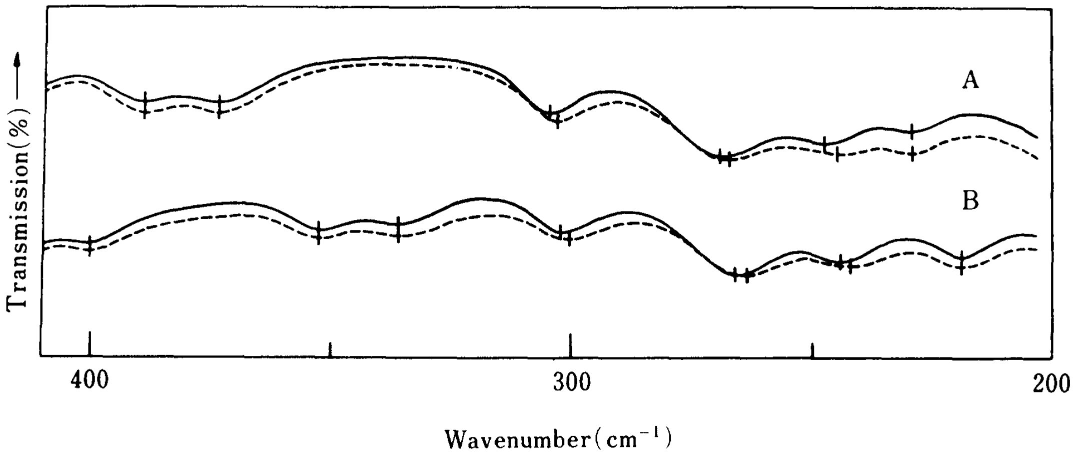

Fig. 2. Expanded IR Spectra of $[Zn(aspn)_2]_n$ and $[Zn(aspn\text{-}d_4)_2]_n$ in the Region between 410 and 200 cm^{-1}

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

In the IR spectrum of $[Zn(aspn)_2]_n$ 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 $[Zn(glutamate)\cdot(H_2O)]_n\cdot(H_2O)_n$,3) 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 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

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

$[^{64}Zn(aspn)_2]_n$ a)	$\Delta\nu_m$ b)	$[^{64}Zn(aspn\text{-}d_4)_2]_n$ 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.

contrast to a large shift on N,N'-deuteration. Accordingly, we assigned three zinc isotope-sensitive bands at 301, 265 and 244 cm^{-1} 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.

The frequency range of the metal-ligand stretching vibrations of $[Zn(aspn)_2]_n$ is lower by about 50 cm^{-1} than those of $[Cu(aspn)_2]_n$.2) 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.3) 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 $[Zn(aspn)_2]_n$, in contrast to the case of $[Cu(aspn)_2]_n$.2) However, the coupling among the Zn-ligand stretching vibrations is not general for the zinc-amino acid complexes.

The Zn-ligand stretching frequencies of $[Zn(aspn)_2]_n$ are consistent with those of $[Zn(glutamate)\cdot(H_2O)]_n\cdot(H_2O)_n$3) and $[Zn(glycinate)_2\cdot(H_2O)]_n$.8,9) 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 amino acid complexes. In contrast with our assignment, Jackovitz *et al.*10,11) carried out normal coordinate analysis and assigned the bands around 160 cm^{-1} to the Zn–O stretching vibrations in their comprehensive studies of metal-amino acid complexes. Our conclusion suggests that the stretching force constant for Zn-O bonds is probably much larger than that assumed by them.

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