[Chem. Pharm. Bull.
31(11)3802—3810(1983)]

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

JUNICHI ODŌ,[a] MASAAKI NISHIO,[a] YUTAKA SAITO,[a] YOSHIMASA TANAKA,*,[a]
and KATSUNOSUKE MACHIDA[b]

Faculty of Pharmaceutical Sciences, Okayama University,[a] 1-1, Tsushima-Naka 1-chome, Okayama 700, Japan and Faculty of Pharmaceutical Sciences, Kyoto University,[b] Sakyo-ku, Kyoto 606, Japan

(Received April 11, 1983)

The infrared spectra of bis(L-serinato)copper(II) and -zinc(II) and their isotopic complexes containing metal and hydrogen isotopes have been measured in the region between 4000 and 200 cm^{-1}. By referring to the isotope shifts, four bands of the Cu complex at 375, 327, 307, and 255 cm^{-1} have been assigned to the Cu–OOC and the Cu–NH_2 stretching vibrations. Two bands of the Zn complex at 230 and 295 cm^{-1} have been assigned to Zn–OOC and Zn–NH_2 stretching vibrations, respectively. By comparing the Cu complex with the Zn complex, the vibrations of two anisostructural serinates included in the Zn complex have been distinguished from each other. The structural difference between the two serinates was clearly reflected in the COO deformation vibrations. The Raman measurement for a single crystal of the Zn complex revealed rather small factor group splittings. A normal coordinate analysis for the Zn complex was carried out by using a complete molecular conformation and an intermolecular force field. The result is consistent with the empirical assignments and the experimental isotope shifts.

Keywords——IR spectra; aminoacid; isotope effect; ^{63}Cu–^{65}Cu substitution; ^{64}Zn–^{68}Zn substitution; bis(L-serinato)copper; bis(L-serinato)zinc; normal coordinate analysis; intermolecular force; intramolecular force

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 state[3-5)] 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.

The present paper 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 our assignments, normal coordinate analysis for the Zn complex was carried out by using a complete molecular conformation and the inter- and intramolecular force fields.

Experimental

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 infrared (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., U.S.A.) 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.

Measurements——The IR spectra were recorded on a JASCO DS-403G IR spectrophotometer (4000—200 cm^{-1}). The measurements were made for the 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.

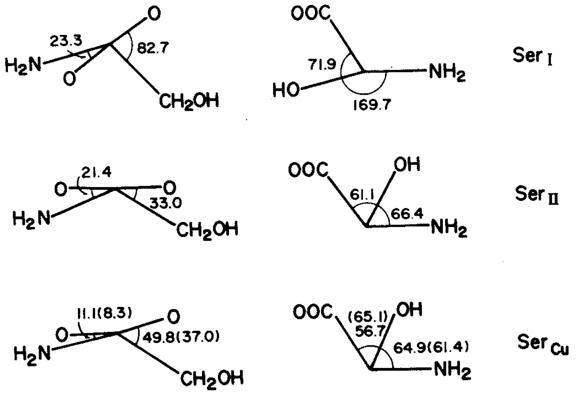

Fig. 1. Structures of L-Serinate in Cu(ser)$_2$ and Zn(ser)$_2$

Normal Coordinate Analysis for Zn(ser)$_2$

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 reported in the previous paper.[16] 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-serine[17] and the constants concerned with the copper atom from Cu(DL-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

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*	*H*(OC′O)	0.06	*H*(ZnNH)	0.10*	*F*(OC′O)	4.00*	*F*(ZnNH)	0.05*
K(C–C′)	2.13	*H*(OC′C)	0.35*	*H*(ZnNC)	0.05	*F*(OC′C)	0.70	*F*(ZnNC)	0.10
K(C–H)	4.20*	*H*(C′CN)	0.65	*H*(OC″C)	0.45*	*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*	*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*	*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*
K(C″–H)	4.09	*H*(C″CH)	0.16	*H*(OZnN)[b)]	0.05	*F*(C″CH)	0.40	*F*(OZnN)[b)]	0.05*
K(O–H)	6.00*	*H*(CNH)	0.34	*H*(OZnN)	0.05*	*F*(CNH)	0.50	*F*(OZnN)	0.05*
K(Zn–O)	0.20*	*H*(HNH)	0.50*	*H*(O′ZnO)	0.05*	*F*(HNH)	0.02	*F*(O′ZnO)	0.05*
K(Zn–N)	0.40*	*H*(CC″H)	0.245	*H*(O′ZnN)	0.05*	*F*(CC″H)	0.502	*F*(O′ZnN)	0.05*
K(Zn–O′)	0.35*	κ(C′)[c)]	0.0*	κ(C″)[c)]	0.0*	κ(N)[c)]	−0.05*		

Valence type force constants[a)] (mdyn·Å/rad²)

f(ωCO₂, ωCO₂)	1.92	*f*(τCC′, τCC′)	0.05	*f*(τCN, τCN)	0.10*	*f*(τCC″, τCC″)	0.05
f(τOH, τOH)	0.004*						

a) C, C′ and C″ denote the methine, the carboxylate and the methylene carbon atoms, respectively.
b) Force constant concerned in the chelate ring.
c) mdyn·Å.
* Refined value.

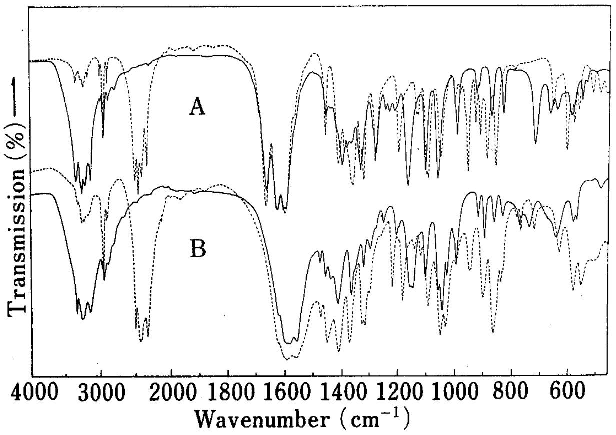

Fig. 2. IR Spectra of Cu(ser)$_2$, Cu(ser-d_3)$_2$, Zn(ser)$_2$ and Zn(ser-d_3)$_2$ in the Region above 450 cm^{-1}

A, Cu(ser)$_2$ (——) and Cu(ser-d_3)$_2$ (----); B, Zn(ser)$_2$ (——) and Zn(ser-d_3)$_2$ (----).

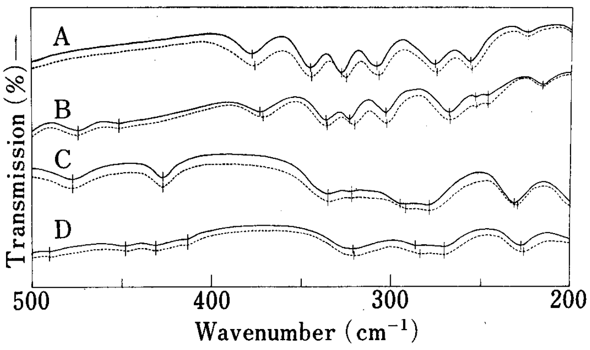

Fig. 3. Expanded IR Spectra of Cu(ser)$_2$, Cu(ser-d_3)$_2$, Zn(ser)$_2$ and Zn(ser-d_3)$_2$ in the Region between 500 and 200 cm^{-1}

A, ^{63}Cu(ser)$_2$ (——) and ^{65}Cu(ser)$_2$ (----); B, ^{63}Cu(ser-d_3)$_2$ (——) and ^{65}Cu(ser-d_3)$_2$ (----); C, ^{64}Zn(ser)$_2$ (——) and ^{68}Zn(ser)$_2$ (----); D, ^{64}Zn(ser-d_3)$_2$ (——) and ^{68}Zn(ser-d_3)$_2$ (----).

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.

Vibrational 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*

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 200 cm^{-1}

Cu(ser)$_2$	Zn(ser)$_2$		Assign.$^{c)}$
IR$^{a)}$	IR$^{a)}$	Calc.$^{b)}$	
3350 vs	3315 vs	3375	νOH(II)
—$^{f)}$		3353	νOH(I)
—$^{f)}$	3240 vs	3194	ν_{a}NH$_2$(I)
3255 vs 3205 vs	3220 sh	3188	ν_{a}NH$_2$(II)
—$^{f)}$	3125 vs	3139	ν_{s}NH$_2$(I)
3125 vs		3133	ν_{s}NH$_2$(II)
—$^{f)}$	2965 sh	2975	νCH(I)
2980 vw		2965	νCH(II)
2935 m	2930 m	2956	ν_{a}CH$_2$(II)
—$^{f)}$		2941	ν_{a}CH$_2$(I)
2875 vw	2875 sh	2927	ν_{s}CH$_2$(II)
—$^{f)}$		2909	ν_{s}CH$_2$(I)
1660 vs	1630 sh		Combination- or over-tone
1626 vs 1605 vs	1590 vs	1616	ν_{a}CO$_2$(II)
—$^{f)}$	1558 vs	1604	ν_{a}CO$_2$(I)
1596 vs	1530$^{d)}$ w	1536	βNH$_2$(II)
—$^{f)}$		1532	βNH$_2$(I)
—$^{f)}$	1472 w	1490	βCH$_2$(I)
1452 m	1452 w	1465	βCH$_2$(II)
1438 vw	1437 w		Combination- or over-tone
—$^{f)}$	1411 m	1415	ν_{s}CO$_2$(I)
1396 m		1412	ν_{s}CO$_2$(II)
1364 vw	1363 m	1354	δCH′(II)
—$^{f)}$	1351 sh	1336	tNH$_2$(I)
—$^{f)}$		1330	δCH′(I)
1331 m	1319 m	1312	tNH$_2$(II)
—$^{f)}$	1295 w	1294	ωCH$_2$(I)
1285 sh 1275 m	1270 w	1274	ωCH$_2$(II)
—$^{f)}$	1245 w	1243	tCH$_2$(I)
1240 w		1238	tCH$_2$(II)
—$^{f)}$	1199 m	1216	δOH(I)
1162 s	1190 sh	1193	δOH(II)
—$^{f)}$	1152 m	1156	ωNH$_2$(I)
1228 w 1208 w	1142 m	1148	ωNH$_2$(II)
1100 m	1120 sh	1117	δCH(II)
1100 m	1098 m	1101	νskel(II)
—$^{f)}$		1098	δCH(I)
—$^{f)}$	1052 m	1091	νskel(I)
1056 m	1039 s	1043	νskel(II)

Cu(ser-d_3)$_2$	Zn(ser-d_3)$_2$		Assign.$^{c)}$
IR$^{a)}$	IR$^{a)}$	Calc.$^{b)}$	
—$^{f)}$	2980 sh	2975	νCH(I)
2995 vw	2960 m	2965	νCH(II)
2960 m 2940 m		2956	ν_{a}CH$_2$(II)
—$^{f)}$		2941	ν_{a}CH$_2$(I)
2880 w	2910 w	2927	ν_{s}CH$_2$(II)
—$^{f)}$	2890 sh	2909	ν_{s}CH$_2$(I)
2490 vs	2500 vs	2451	νOD(II)
—$^{f)}$		2436	νOD(I)
—$^{f)}$	2435 vs	2351	ν_{a}ND$_2$(I)
2445 vs 2440 vs	2430 sh	2347	ν_{a}ND$_2$(II)
—$^{f)}$	2390 sh	2271	ν_{s}ND$_2$(I)
2320 vs	2335 vs	2267	ν_{s}ND$_2$(II)
1660 vs	1630 sh		Combination- or over-tone
1624 vs 1597 vs	1592 vs	1615	ν_{a}CO$_2$(II)
—$^{f)}$	1558 vs	1604	ν_{a}CO$_2$(I)
—$^{f)}$	1472 m	1490	βCH$_2$(I)
1452 m	1450 m	1465	βCH$_2$(II)
—$^{f)}$	1409 m	1416	ν_{s}CO$_2$(I)
1410 m		1412	ν_{s}CO$_2$(II)
1353 s	1369 m	1341	δCH′(II)
—$^{f)}$	1324 m	1326	δCH′(I)
1328 m 1315 m	1313 m	1296	ωCH$_2$(II)
—$^{f)}$	1297 sh	1287	ωCH$_2$(I)
—$^{f)}$	1275 sh	1260	tCH$_2$(I)
1275 m	1256 sh	1242	tCH$_2$(II)
1191 m	1217 m	1199	δCH(II)
—$^{f)}$	1180 m	1187	δCH(I)
—$^{f)}$	1139 w	1147	βND$_2$(I)
1130 m 1122 m	1117 w	1128	βND$_2$(II)
1093 m 1085 m	1090 m	1084	νskel(II)
—$^{f)}$		1087	νskel(I)
—$^{f)}$	1048 m	1061	tND$_2$(I)
1045 m		1058	νskel(II)
		1037	tND$_2$(II)
—$^{f)}$	1029 m	1019	νskel(I)
—$^{f)}$	994 w	987	νskel(I)
945 m	947 m	963	νskel(II)
—$^{f)}$		957	δOD(I)
993 w 975 w	943 sh	949	δOD(II)

Table II (continued)

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]	
—[f]	1023 m	1029	νskel(I)	—[f] 919 m 901 m	898 m	883 903	νskel(I) νskel(II)
—[f]	1000 sh	997	νskel(I)	875 m	862 m	872	ωND$_2$(II)
995 sh 987 m	994 m	995	νskel(II)				
—[f]		979	νskel(I)	—[f]	855 sh	856	ωND$_2$(I)
930 m 912 sh	912 m	932	νskel(II)	—[f]	844 w	805	ρCH$_2$(I)
—[f]	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)	—[f]	762 m	750	ωCO$_2$(I)
—[f]	764 m	754	ωCO$_2$(I)	—[f]	714 m	726	βCO$_2$(I)
—[f]	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)	—[f]	549 m	550	ρCO$_2$(I)
—[f]	654 sh	654	ρNH$_2$(I)	552 m	545 sh	547	ρCO$_2$(II)
631 m	572 m	601	δskel(II)	—[f]	510 w	526	ρND$_2$(I)
—[f]	556 m	566	ρCO$_2$(I)	506 m	490 w	479	ρND$_2$(II)
500 vw	510 vw	526	ρCO$_2$(II)	565 m 587 m	449 w	474	δskel(II)
581 m	478 w	478	δskel(II)	—[f]	432 w	426	δskel(I)
530 vw 545 w		449	δskel(II)	475 m 452 w	415 w	396	δskel(II)
—[f]	425 w	424	δskel(I)	336 w	320 w	324	δskel
344 w	334 w	357	δskel			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 sh	270	νMe-ligand
377 w	295 sh	276	νMe-ligand	267 w	—[e]	249	δskel
275 w	250[d] 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	198[d] w	207	δskel	214 vw	—[e]	190	δskel

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.
b) Species A.
c) ν, stretching; β, bending; δ, deformation; *t*, twisting; ω, wagging; ρ, rocking.
d) Raman frequency.
e) Not observed.
f) Not expected.

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

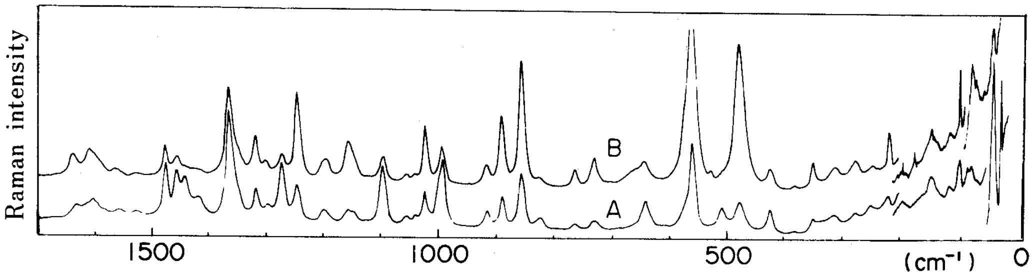

Fig. 4. Polarized Raman Spectra of Zn(ser)$_2$ Single Crystal
A, a(ba)b; B, a(bc′)b.

ser$_\mathrm{I}$ and ser$_\mathrm{II}$, the polarized 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$_\mathrm{I}$ and ser$_\mathrm{II}$, and should not arise from the factor group splitting. In the IR spectra between 800 and 720 cm^{-1}, Cu(ser)$_2$ shows no bands but replacement of the Cu atom 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$_\mathrm{I}$ 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$_\mathrm{II}$. 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$_\mathrm{I}$ and ser$_\mathrm{II}$ 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] we tentatively assigned the three bands at 344, 275 and 223 cm^{-1} 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, 315, 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 ^{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

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	*ca.* 0	δskel
223 vw	0	214 w	0	δskel

a) m, medium; 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.

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}

$Zn(ser)_2$				$Zn(ser\text{-}d_3)_2$				Assignments[c]
Obs.[a]	Calc.	$\Delta\nu_m$[b] Obs.	$\Delta\nu_m$[b] Calc.	Obs.[a]	Calc.	$\Delta\nu_m$[b] Obs.	$\Delta\nu_m$[b] 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
321 vw	329	0	0.2		308	0	0.2	δskel
295 sh	276	*ca.* 3	2.9	285 sh	270	*ca.* 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; vw, very weak; sh, shoulder.
b) Shifts of band center on ^{64}Zn–^{68}Zn substitution.
c) ν, stretching; δ, deformation.
d) Raman frequency.
e) Not observed.

vibration and the Zn–O asymmetrical stretching vibration, respectively. The remaining bands were assigned to the skeletal deformation vibrations by referring to the frequency shifts on *N,O*-deuteration and the initial calculation. The conformational difference between ser_I and 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.

Discussion

As shown in Table IV, the final calculation reproduced well the observed isotope shifts on ^{64}Zn–^{68}Zn substitution, supporting our assignments. 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

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-d_3)$_2$		Bands[b]
Obs.[a]	Calc.[a]	Obs.[a]	Calc.[a]	
−32	−12	−34	−11	$\nu_a CO_2$
0[c]	−4	22	19	$\beta NH_2(ND_2)$
20	25	22	25	βCH_2
0	3	0	4	$\nu_s CO_2$
−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	20	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.

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-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.

Acknowledgments The authors are very grateful to Dr. Tsuneyuki Higashi of Kyoto University for taking the X-ray photograph. The calculations were carried out by using the FACOM M-190 computer at the Data Processing Center of Kyoto University and the ACOS 1000 computer of Okayama University Computer Center. This study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References and Notes

1) I. Harada, *Tanpakushitu Kakusan Koso*, **24**, 1441 (1979).
2) J. F. Chlebowski and J. E. Coleman, "Metal Ions in Biological Systems," Vol. 6, ed. by H. Sigel, Marcel Dekker, Inc., New York, 1976, pp. 1—140.
3) P. G. Jönsson and A. Kvick, *Acta Crystallogr., Sect. B*, **28**, 1827 (1972).
4) H. J. Shimpson and R. E. March, *Acta Crystallogr.*, **20**, 550 (1966).
5) M. N. Frey, M. S. Lehmann, T. F. Koetzle, and W. C. Hamilton, *Acta Crystallogr., Sect. B*, **29**, 876 (1973).
6) A. Dijkstra, *Acta Crystallogr.*, **20**, 588 (1966).

7) R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *J. Chem. Soc. (A)*, **1969**, 1864.
8) D. van der Helm and C. E. Tatsch, *Acta Crystallogr., Sect. B*, **28**, 2307 (1972).
9) D. van der Helm, M. B. Lawson, and E. L. Enwall, *Acta Crystallogr., Sect. B*, **27**, 2411 (1971).
10) B. Evertson, *Acta Crystallogr., Sect. B*, **25**, 30 (1969).
11) F. S. Stephens, R. S. Vagg, and P. A. Williams, *Acta Crystallogr., Sect. B*, **31**, 841 (1975).
12) F. S. Stephens, R. S. Vagg, and P. A. Williams, *Acta Crystallogr., Sect. B*, **33**, 433 (1977).
13) H. C. Freeman, *Adv. Protein Chem.*, **22**, 257 (1967).
14) D. van der Helm, A. F. Nicholas, and C. G. Fisher, *Acta Crystallogr., Sect. B*, **26**, 1172 (1970).
15) D. van der Helm and W. A. Franks, *Acta Crystallogr., Sect. B*, **25**, 451 (1969).
16) J. Odō, M. Nishio, Y. Saito, Y. Tanaka, and K. Machida, *Chem. Pharm. Bull.*, **31**, 2967 (1983).
17) K. Machida, M. Izumi, and A. Kagayama, *Spectrochim. Acta*, **35A**, 1333 (1979).
18) Y. Inomata, T. Inomata, and T. Moriwaki, *Bull. Chem. Soc. Jpn.*, **44**, 365 (1971).
19) K. Machida, A. Kagayama, Y. Saito, and Y. Kuroda, *Spectrochim. Acta*, **33A**, 569 (1977).
20) K. Machida, A. Kagayama, Y. Saito, and T. Uno, *Spectrochim. Acta*, **34A**, 909 (1978).
21) K. Machida, A. Kagayama, and Y. Saito, *J. Raman Spectrosc.*, **7**, 188 (1978).
22) K. Machida, A. Kagayama, and Y. Saito, *J. Raman Spectrosc.*, **8**, 133 (1979).
23) G. W. R. Canham and A. B. P. Lever, *Spectrosc. Lett.*, **6**, 109 (1973).
24) R. S. Krishnan, V. N. Sankaranarayanan, and K. Krishnan, *J. Indian Inst. Sci.*, **55**, 66 (1973).