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Metal Isotope Effects on the Vibrational Spectra of Polymeric Metal Complexes. IV.[1] Infrared Spectra of *trans*- and *cis*-[Bis(D-alaninato)copper(II)]

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The infrared spectra of *trans*- and *cis*-[bis(D-alaninato)copper(II)]$_n$ and their isotopic complexes containing ^{63}Cu, ^{65}Cu and deuterium were measured in the region between 4000 and 200 cm^{-1}. By referring to the isotope shifts on deuteration and ^{63}Cu and ^{65}Cu substitution, the bands around 370 and 320 cm^{-1} were assigned to the Cu–N and the Cu–O asymmetric stretching vibrations, respectively, for both the *trans* and *cis* complexes. The magnitudes of the copper isotope shifts are consistent with those calculated from the normal coordinate analysis by using a complete molecular conformation and an intermolecular force field. The *trans*-isomer showed three copper isotope sensitive bands, while the *cis*-isomer showed two.

Keywords——IR spectra; aminoacid; alanine; *trans-cis* isomerism; [bis(alaninato)copper(II)]; ^{63}Cu–^{65}Cu substitution; normal coordinate analysis; deuteration; isotope shift; intramolecular force; intermolecular force

The copper alaninate complex is known to take a *trans* or a *cis* conformation[2,3] 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.[4] Herlinger *et al.* tried to identify the differences of the Cu-ligand stretching vibrations between the *trans* and the *cis* complexes.[5] Recently, Percy and Stenton assigned the Cu-ligand stretching bands of *trans*-bis-L-alaninatocopper by means of ^{18}O- and ^{15}N-substitutions[6] 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.

The present paper deals with infrared (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

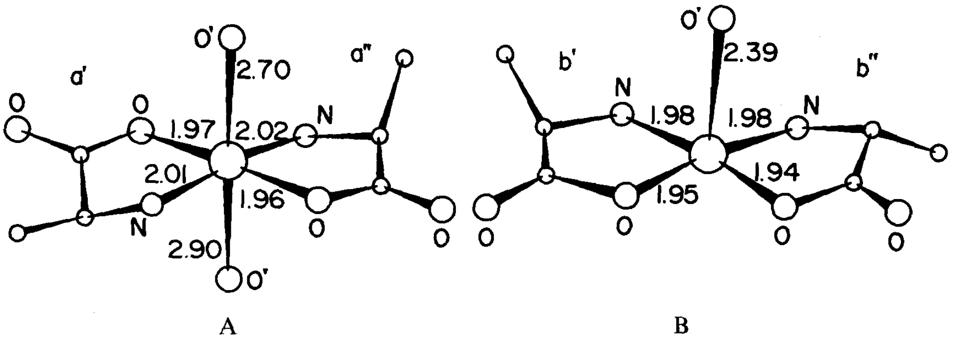

Fig. 1. Structures and Bond Lengths[2,3] of t-Cu(ala)$_2$ (A) and c-Cu(ala)$_2$ (B)

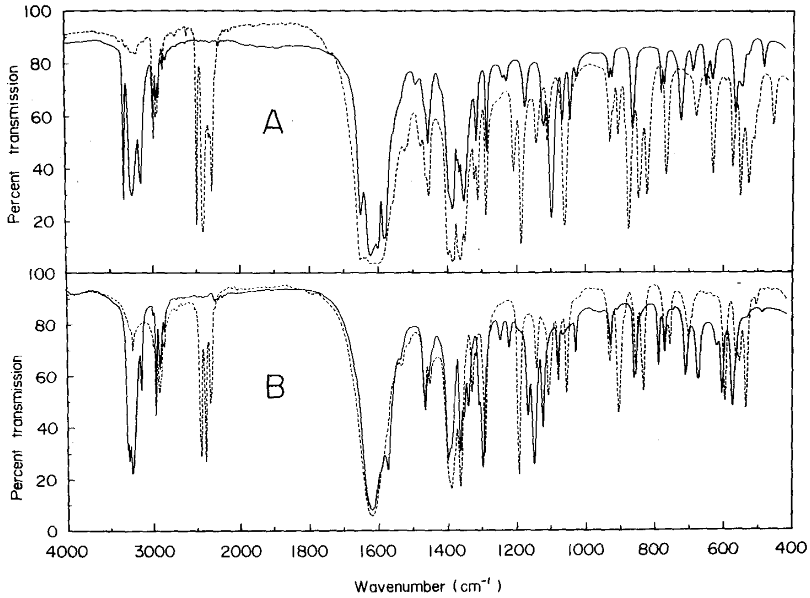

Fig. 2. IR Spectra of t-Cu(ala)$_2$, t-Cu(ala-d_2)$_2$, c-Cu(ala)$_2$ and c-Cu(ala-d_2)$_2$ in the Region above 400 cm^{-1}

A, t-Cu(ala)$_2$ (——) and t-Cu(ala-d_2)$_2$ (------); B, c-Cu(ala)$_2$ (——) and c-Cu(ala-d_2)$_2$ (------).

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 the intermolecular forces to confirm the empirical assignments.

Experimental

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.[2] 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., U.S.A.) in the same manner as reported previously.[7] 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 3 d on a boiling water bath.[8] The isotopic purities were 99.89% for ^{63}CuO and 99.70% for ^{65}CuO.

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.,

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.[6]	$\Delta^{18}O$ Obs.[6]	Calc.[b]	$\Delta^{15}N$ Calc.	$\Delta^{18}O$ Calc.	Assignments[c]
3281 s	—[d]	—[d]	3292 a′	8.9	0.0	$\nu_a\mathrm{NH_2}$
3276 s	—[d]	—[d]	3286 a″	8.8	0.0	$\nu_a\mathrm{NH_2}$
3240 s	—[d]	—[d]	3232 a′	4.6	0.0	$\nu_s\mathrm{NH_2}$
3133 s	—[d]	—[d]	3230 a″	4.7	0.0	$\nu_s\mathrm{NH_2}$
2973 m	—[d]	—[d]	2976 a″	0.0	0.0	$\nu_s\mathrm{CH_3}$ or $\nu_d\mathrm{CH_3}$ or $\nu\mathrm{CH}$
			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	$\nu_a\mathrm{CO_2}$
			1633 a″	0.2	22.9	$\nu_a\mathrm{CO_2}$
1573 vs	3	[e]	1621 a′	3.1	4.5	$\beta\mathrm{NH_2}$
			1573 a″	3.2	0.3	$\beta\mathrm{NH_2}$
1463 m	—[d]	—[d]	1499 a′	0.2	0.1	$\delta_d\mathrm{CH_3}$
			1457 a″	0.0	0.0	$\delta_d\mathrm{CH_3}$
1452 sh	[e]	[e]	1454 a″	0.1	0.1	$\delta_d\mathrm{CH_3}$
			1450 a′	0.1	0.1	$\delta_d\mathrm{CH_3}$
1395 s	[e]	—[d]	1380 a′	0.6	28.8	$\nu_s\mathrm{CO_2}$
1364 s	1.5	10	1373 a″	0.1	22.2	$\nu_s\mathrm{CO_2}$
1387 sh	—[d]	—[d]	1388 a″	0.3	3.9	$\delta_s\mathrm{CH_3}$
			1363 a′	0.4	4.6	$\delta_s\mathrm{CH_3}$
1306 w	[e]	9	1348 a″	1.6	10.5	$\delta\mathrm{CH}$
1296 s	1.5	13	1338 a′	1.0	11.6	$\delta\mathrm{CH}$
1354 sh	[e]	[e]	1306 a″	2.1	1.9	$\delta\mathrm{CH}$
1339 m	2	[e]	1300 a′	1.6	1.9	$\delta\mathrm{CH}$
1245 w	[e]	[e]	1248 a′	1.0	0.3	$t\mathrm{NH_2}$
1220 w	[e]	2	1213 a″	2.0	0.6	$t\mathrm{NH_2}$
1165 m	6	4.5	1161 a″	5.8	1.2	$\omega\mathrm{NH_2}$
1149 s	5	4.5	1150 a′	7.3	1.5	$\omega\mathrm{NH_2}$
1119 s	6.5	1.5	1138 a′	4.3	1.6	$\nu\mathrm{CN}$
			1114 a″	5.2	1.6	$\nu\mathrm{CN}$
1078 m	3	2.5	1043 a′	0.9	5.9	$\rho\mathrm{CH_3}$
1026 m	2	2.5	1026 a″	0.1	4.7	$\rho\mathrm{CH_3}$
970 vw	—[d]	—[d]	981 a″	0.3	1.6	$\rho\mathrm{CH_3}$
			972 a′	0.3	0.7	$\rho\mathrm{CH_3}$
925 m	4.5	5.5	913 a″	2.9	5.1	νskel
			903 a′	2.7	4.5	νskel
856 m	3.5	—[d]	878 a″	2.1	12.5	νskel
850 m	2.5	—[d]	850 a′	4.2	17.2	νskel
786 m	[e]	8	775 a′	1.0	6.4	$\omega\mathrm{CO_2}$
767 m	[e]	5	750 a″	0.1	6.4	$\omega\mathrm{CO_2}$
706 m	1.5	11	721 a″	2.3	12.9	$\beta\mathrm{CO_2}$
618 w	—[d]	—[d]	623 a′	2.8	8.9	$\beta\mathrm{CO_2}$
672 m	5	2	720 a′	3.0	0.2	$\rho\mathrm{NH_2}$
			677 a″	4.9	0.3	$\rho\mathrm{NH_2}$
602 m	2.5	12	571 a′	9.0	8.6	$\rho\mathrm{CO_2}$
571 m	7.5	7	557 a″	7.3	11.6	$\rho\mathrm{CO_2}$
562 sh	—[d]	—[d]	518 a′	4.1	13.1	δskel

t-Cu(ala-d_2)$_2$

Obs.[a]	Calc.[b]	Assignments[c]
2970 m	2976 a′	$\nu_s\mathrm{CH_3}$ or $\nu_d\mathrm{CH_3}$ or $\nu\mathrm{CH}$
	2938 a″	
2931 m	2898 a′	
	2873 a′	
	2872 a″	
	2869 a″	
2867 m	2790 a′	
	2778 a″	
2450 s	2424 a′	$\nu_a\mathrm{ND_2}$
2405 s	2418 a″	$\nu_a\mathrm{ND_2}$
2345 s	2338 a′	$\nu_s\mathrm{ND_2}$
	2337 a″	$\nu_s\mathrm{ND_2}$
1619 vs	1642 a′	$\nu_a\mathrm{CO_2}$
	1632 a″	$\nu_a\mathrm{CO_2}$
1461 m	1503 a′	$\delta_d\mathrm{CH_3}$
	1457 a″	$\delta_d\mathrm{CH_3}$
1447 w	1454 a″	$\delta_d\mathrm{CH_3}$
	1450 a′	$\delta_d\mathrm{CH_3}$
1385 s	1377 a′	$\nu_s\mathrm{CO_2}$
	1373 a″	$\nu_s\mathrm{CO_2}$
1390 sh	1386 a″	$\delta_s\mathrm{CH_3}$
	1362 a′	$\delta_s\mathrm{CH_3}$
1358 s 1326 m 1288 m	1336 a″	$\delta\mathrm{CH}$
	1330 a′	$\delta\mathrm{CH}$
	1264 a′	$\delta\mathrm{CH}$
	1246 a″	$\delta\mathrm{CH}$
1190 s	1203 a′	$\beta\mathrm{ND_2}$
	1171 a″	$\beta\mathrm{ND_2}$
1141 m	1118 a′	$\nu\mathrm{CN}$
	1101 a″	$\nu\mathrm{CN}$
1107 m	1085 a′	$\rho\mathrm{CH_3}$
1076 m	1058 a″	$\rho\mathrm{CH_3}$
1050 m	1047 a″	$\rho\mathrm{CH_3}$
	1025 a′	$\rho\mathrm{CH_3}$
926 m	930 a″	$t\mathrm{ND_2}$
	919 a′	$t\mathrm{ND_2}$
905 m	910 a″	νskel
	900 a′	νskel
853 m	878 a′	$\omega\mathrm{ND_2}$
	869 a″	$\omega\mathrm{ND_2}$
830 m	839 a′	νskel
	824 a″	νskel
765 m	759 a′	$\omega\mathrm{CO_2}$
751 m	747 a″	$\omega\mathrm{CO_2}$
700 m	706 a″	$\beta\mathrm{CO_2}$
596 m	609 a′	$\beta\mathrm{CO_2}$
563 m	544 a′	$\rho\mathrm{ND_2}$
533 m	520 a″	$\rho\mathrm{ND_2}$
553 m	565 a″	$\rho\mathrm{CO_2}$
	553 a′	$\rho\mathrm{CO_2}$
503 vw	497 a′	δskel

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}.

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 frequency 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

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′	
3130 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′	$\nu_s ND_2$
	2784 b′		2305 s	2318 b″	$\nu_s ND_2$
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″	$\delta_d CH_3$
1490 w	1471 b′	$\delta_d CH_3$	1452 m	1452 b′	$\delta_d CH_3$
	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″	νskel
1043 m	1022 b′	ρCH_3	905 m	923 b′	νskel
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′	νskel	844 m	872 b″	ωND_2
920 w	903 b″	νskel		864 b′	ωND_2
860 m	873 b′	νskel	818 m	840 b″	νskel
	863 b″	νskel		820 b′	νskel
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″	δskel	500 sh	483 b″	δskel

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.

in Fig. 3. The observed frequencies are listed in Tables I and II together with approximate intensities, assignments and calculated frequencies.

Normal Coordinate Analyses

According to the X-ray analyses,[2,3] 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[9] 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 Ewald's method as described by Hiraishi.[10] 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.*[3] and partially modified coordinates[2,11] of Cu(L-ala)$_2$ were used for *t*-Cu(ala)$_2$. A modified Urey–Bradley type 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.[12] 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.*[13] 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 Cu–O′ 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.*[6] 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,[12,14–17] 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

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/red^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.

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.[15)] 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 $K=0.2$. A list of the atomic charges and coordinates together with the details of the calculated results is available from the authors on request.

Vibrational 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,[4-6,12,13,18)] 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.*[6)] 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 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.

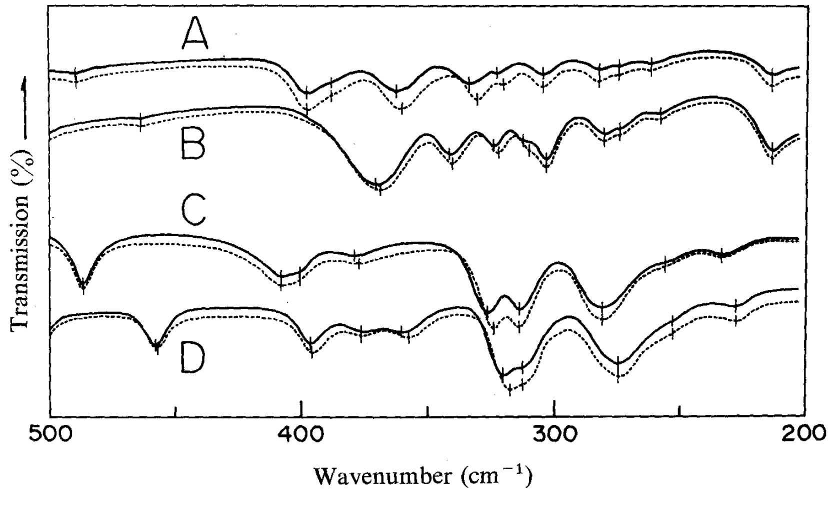

Fig. 3. Expanded IR Spectra of t-Cu(ala)$_2$, t-Cu(ala-d_2)$_2$, c-Cu(ala)$_2$ and c-Cu(ala-d_2)$_2$ in the Region between 500 and 200 cm^{-1}

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)$_2$ (------).

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)$_2$					Assignments[e]
Obs.[a]	Calc.[b]	$\Delta^{15}N$		$\Delta^{18}O$		Δm			Obs.[a]	Calc.[b]	Δm			
		Obs.[6]	Calc.	Obs.[6]	Calc.	Obs.	Calc.				Obs.	Calc.		
							I[c]	II[d]				I[c]	II[d]	
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	—[f]	2.2	—[f]	5.2	*ca.* 0	0.2	0.2		383		0.5	0.9	δskel
361 m	379	[g]	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	*ca.* 3	3.2	3.0	310 sh	329	*ca.* 2	1.7	1.2	ν_aCu–OOC
303 m	283	[g]	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	—[f]	0.7	—[f]	3.4	*ca.* 0	0.3	0.1	271 sh	255	*ca.* 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] Calculation I by using only the intramolecular forces.
[d] Calculation II by using the intra- and intermolecular forces.
[e] ν, stretching; δ, deformation.
[f] Not reported.
[g] 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)$_2$					Assignments[f]
		Δm[c]					Δm[c]			
Obs.[a]	Calc.[b]	Obs.	Calc.		Obs.[a]	Calc.[b]	Obs.	Calc.		
			I[d]	II[e]				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	*ca.* 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	*ca.* 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.

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, we assigned the 361 cm^{-1} band 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 Stenton[6] 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.*[5] and Percy *et al.*[6] In this work, 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 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 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, we tentatively assigned the bands at 483 and 400 cm^{-1} 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 assignment.

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 re-distribution 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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