BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 365—372 (1971)

Infrared Absorption Spectra and Normal Coordinate Analysis of Metal-DL-α-Serine Chelates

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(Received September 1, 1970)

The infrared absorption spectra of DL-α-serine and four metal-DL-α-serine chelates have been investigated from 4000 to 200 cm^{-1}. A normal coordinate analysis has been accomplished for the metal chelates as a 27-body problem and an approximate description of the vibrational mode has been assigned to the observed frequencies. The frequency separation between carboxylate antisymmetric and symmetric stretching vibrations and values of the bond-stretching force constants for the metal-nitrogen bonds have been found to decrease in the order Pt(II)>Pd(II)>Cu(II)>Ni(II). These facts show that the hydroxy group in the β-position of DL-α-serine has no influence on the order of metal-ligand bond strength, which order has been already found in aliphatic α-amino acids chelates having no hydroxy group in the β-position. Two species of copper chelates have been prepared. Though the infrared spectrum of one of them is similar to that of the nickel(II) chelate, that of the other species is different. This fact may be explained by assuming that the copper ion has been coordinated with the hydroxy group in the latter.

The infrared absorption spectra and the normal coordinate analysis for aliphatic α-amino acid chelates have already been studied by Lane$^{1)}$ and Walter$^{2-4)}$. However, DL-α-serine having hydroxy group in the β-position and its metal-chelates have not been studied yet in detail. Nakamura$^{5)}$ has made some empirical assignments for DL-α-serine copper(II) chelate in the region 1700 to 400 cm^{-1}. Nakamoto$^{6)}$ have demonstrated that in amino acid chelates the frequency separation between carboxylate stretching vibrations increases in the order Ni(II)<Cu(II)<Pd(II)<Pt(II) regardless of the nature of the ligand, if the comparison is made in the same physical state. They have concluded that this fact is based on the increase of the covalent character in metal-oxygen bond. Nakagawa *et al.*$^{2)}$ showed in DL-α-valine chelates that the metal-nitrogen bond-stretching force constants vary in the order Ni(II)<Cu(II)<Pd(II)<Pt(II) which indicates a relative strength of the interaction of metal-nitrogen bond and that the NH$_2$ stretching and the NH$_2$ rocking frequencies follow the same order.

In this investigation, the infrared spectra of four metal-serine chelates have been studied. The bond-stretching force constants for the metal-nitrogen bond have been calculated. In addition, we discuss how the hydroxy group in β-position influences the relation mentioned above. The problem of whether the hydroxy group coordinates with metal ion or not is also taken up.

Experimental

Preparation of Compounds. Bis(DL-α-serino)-platinum(II) was prepared by stirring 2.6 g (0.025 mol) of DL-α-serine and 1.3 g (0.0031 mol) of potassium tetrachloroplatinate(II) in water (50—100 m*l*) at room temperature for several days. The white crystals separated were recrystallized from hot water and dried at room temperature *in vacuo* for several hours.

Found: C, 18.13; H, 2.85; N, 6.80%. Calcd for Pt-$C_6H_{12}N_2O_6$: C, 17.87; H, 3.00; N, 6.95%.

Bis(DL-α-serino)-palladium(II) was prepared by employing essentially the same procedure as that used above for the platinum(II) chelate.

Found: C, 22.38; H, 3.68; N, 8.75%. Calcd for Pd-$C_6H_{12}N_2O_6$: C, 22.91; H, 3.85; N, 8.91%.

Two species of Bis(DL-α-serino)-copper(II) were prepared. Elementary analysis of each of these two species gives the same results, but the absorption spectra and the color of these two chelates are different. One of them which gives a similar spectrum to the nickel(II) chelate was named " A chelate " and the other was named "B chelate".

The A chelate was prepared by stirring 5.3 g (0.05 mol) DL-α-serine and 2.8 g (0.013 mol) of basic copper carbonate in hot water at 70°C for 15 min, then condensing the filtrate to 25 m*l* after filtering. The blue crystal formed was filtered at hot stage. By cooling the filtrate, the sky blue B chelate was obtained. Both precipitates were washed by water and dried for several hours at 50°C *in vacuo*.

These chelates will be discussed in detail below.

A chelate. Found: C, 26.81; H, 4.23; N, 10.29%. Calcd for $CuC_6H_{12}N_2O_6$: C, 26.52; H, 4.45; N, 10.31%.

B chelate. Found: C, 26.89; H, 4.29; N, 10.30%. Calcd for $CuC_6H_{12}N_2O_6$: C, 26.52; H, 4.45; N, 10.31%.

Bis(DL-α-serino)-nickel(II) was prepared from 5.3 g (0.05 mol) of DL-α-serine and 3.0 g (0.008 mol) of nickel carbonate by the same procedure used above for the copper A chelate.

Found: C, 23.74; H, 5.39; N, 9.29%. Calcd for Ni-$C_6H_{12}N_2O_6 \cdot 2H_2O$: C, 23.79; H, 5.32; N, 9.25%.

Deuteration of Compounds. The deuterated DL-α-serine and metal chelates were prepared by dissolving the DL-α-serine and each chelate in 99.75 atom% deuterium oxide at 80°C and drying them *in vacuo*. The NH and OH groups were deuterated by this method.

Thermal Analysis of Chelates. Thermal analysis was performed with Rigaku Denki DTA-8001 from room temperature to 400°C in air and at the same time, the decrease of weight accompanying an endothermic reaction was measured. It was found that only the nickel(II) chelate had two molecules of water.

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1) T. J. Lane, C. S. C., J. A. Durkin, and R. J. Hooper, *Spectrochim. Acta*, **20**, 1017 (1964).

2) I. Nakagawa, R. J. Hooper, and J. L. Walter, C. S. C., *ibid.*, **21**, 1 (1965).

3) J. F. Jackovitz and J. L. Walter, C. S. C., *ibid.*, **22**, 1393 (1966).

4) J. F. Jackovitz, J. A. Durkin, and J. L. Walter, C. S. C., *ibid.*, **23A**, 67 (1967).

5) K. Nakamura, *Nippon Kagaku Zasshi*, **80**, 113 (1959).

6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York (1963), p. 201.

Absorption Measurement. The infrared absorption spectra from 4000 to 200 cm^{-1} were obtained with Hitachi EPI-G$_2$ and EPI-L spectrophotometers and were calibrated with polystylene, 1.2.4-trichlorobenzene and atmospheric water vapor. Samples were prepared as potassium bromide discs and nujol mulls. The spectra are shown in Figs. 1 and 2. The observed absorption frequencies and assignments for DL-α-serine and the metal chelates are listed in Table 1.

Discussion

The assignments of observed frequencies were made by comparison with metal-glycine,[1] -valine,[2] -leucine,[3] and -alanine[4] chelates and DL-α-amino-*n*-butyric acid[7] which had been thoroughly studied.

The spectra of DL-α-serine chelates are similar to the spectra of those which have *trans* configurations. The observed frequencies of DL-α-serine chelates have been reasonably assigned.

Assignment of Observed Frequencies. DL-α-serine: The spectrum of DL-α-serine shows the bands of NH$_3^+$ and COO$^-$ which are characteristic of a zwitter ion as shown in Fig. 1. The strong broad bands at about 2900 cm^{-1} are assigned to the OH, CH and NH$_3^+$ stretching vibrations. On deuteration, the CH stretching vibration band is not shifted and is assigned easily.

The bands at 1662, 1633, 1513 and 1166 cm^{-1} which shift on deuteration are due to NH$_3^+$ deformation vibrations, since no corresponding bands appear in the metal chelates.

In addition there are bands at 1250 and 729 cm^{-1} which disappear on deuteration. Primary alcohols in the bonded state have diffuse association bands near 1420 and 1330 cm^{-1} (OH deformation and CH$_2$ wagging).[8] All alcohols show very broad bands in the range 750—650 cm^{-1}, which are assigned to out-of-plane bonded OH deformation vibrations.[9] It has been generally known that the frequencies of OH deformation vibrations can be affected by structures and hydrogen bond.[9] Therefore, it is reasonable to assign these two bands respectively to the OH in plane and out-of-plane deformation vibrations, considering that these bands appear at the same region also in the metal chelates and that the force constants of OH deformation vibrations calculated by normal coordinate analysis are approximately equal to that already reported for alcohol.

The assignments for COO$^-$ stretching and deformation vibrations and CH and CH$_2$ deformation vibrations are easily made as shown in Table 1. The bands of CH and CH$_2$ deformation vibrations appear in the same region as DL-α-amino-*n*-butyric acid.[7] The hydroxy group is thought not to have affected these deformation vibrations. CN and CC stretching and skeletal deformation vibrations are assigned by comparison with the spectra of the metal chelates. The band at 1030 cm^{-1} is assigned to CO stretching vibration as in methyl alcohol.[9]

Metal-chelates: The spectra of the metal chelates shown in Figs. 1 and 2 are similar to each other except for that of copper(II) B chelate.

3400 to 2800 cm^{-1}: Although the bands above 3000 cm^{-1} are due to NH$_2$ antisymmetric and symmetric stretching and OH stretching vibrations, it is difficult to assign them separately, since all bands shift on deuteration.

1700 to 500 cm^{-1}: In this region the NH$_2$ deformation vibration appears instead of NH$_3^+$ deformation vibration of the ligand. They are assigned in view of the shift in deuterated compounds. The COO$^-$ antisymmetric stretching vibration is observed in higher frequencies and deformation vibrations are at lower frequencies than those of the ligand. The OH in plane deformation vibration occurs at the same region (1250 cm^{-1}) as in the ligand and the OH out-of-plane

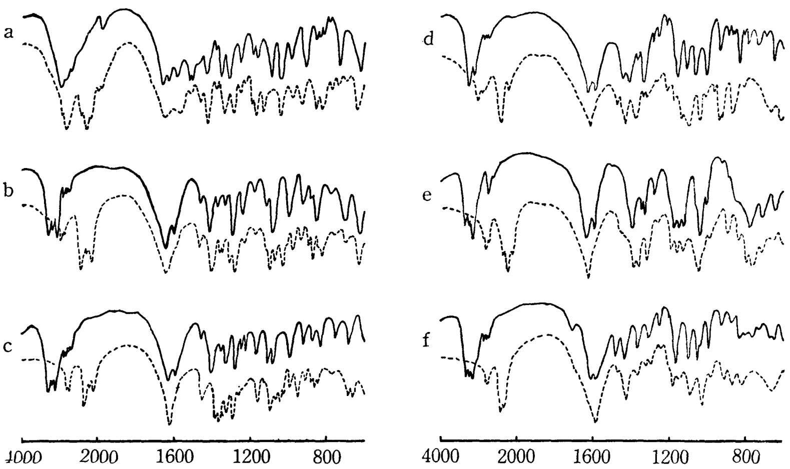

Fig. 1. Infrared absorption spectra of DL-α-serine, its chelates (——) and these deuterated compounds (----) in KBr disks.
a = DL-α-serine, b = Pt(II), c = Pd(II), d = Cu(II) A, e = Cu(II) B, f = Ni(II)

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[7] N. B. Colthup, L. H. Daly, and S.E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York and London (1964), p. 275.

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York (1958), p. 108.

[9] M. Tsuboi and T. Takenishi, "Kagaku no Ryoiki," Zokan 37, Nanko-do, Tokyo (1959), p. 41.

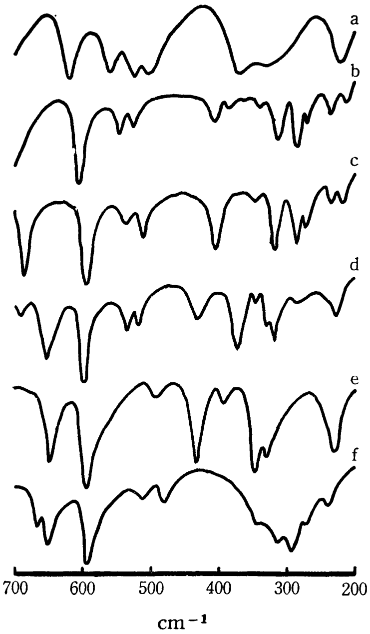

Fig. 2. Infrared absorption spectra of DL-α-serine and its metal chelates in nujol.
a=DL-α-serine, b=Pt(II), c=Pd(II), d=Cu(II) A, e=Cu(II) B, f=Ni(II)

deformation vibration shifts to lower frequencies.

500 to 200 cm^{-1}: In this region the absorption bands which cannot be observed in the ligand appear at 404 cm^{-1} for platinum(II) chelate, 407 cm^{-1} for palladium(II) chelate, 373 cm^{-1} for copper(II) A chelate, 394 cm^{-1} for copper(II) B chelate and 350 cm^{-1} for nickel(II) chelate. They are assigned to metal-nitrogen stretching vibration. The bands at 217 cm^{-1} for platinum(II) chelate and 218 cm^{-1} for palladium(II) chelate are assigned to metal-oxygen stretching vibration. Nakamura[5] has assigned the bands at 588 cm^{-1} for DL-α-serine copper(II) chelate and 581 cm^{-1} for DL-α-alanine copper(II) chelate to copper-nitrogen stretching vibration, and the bands at about 420 cm^{-1} to COO^- rocking vibration. These assignments are different from ours. If the band at about 590 cm^{-1} is assigned to metal-nitrogen stretching vibration, the force constant of metal-nitrogen stretching vibration has the value of 1.8—2.0 mdyn/Å by the calculation, which is much larger than that for glycine[1] and valine[2] chelates. In addition NH_2 vibrations for serine chelate are at the same region as those for valine chelate.[2] Therefore it is doubtful to assign the band at about 590 cm^{-1} to metal-nitrogen stretching vibration. The metal-nitrogen stretching vibration was observed in the region from 400 to 360 cm^{-1} and the NH_2 stretching vibration in the region from 3300 to 3100 cm^{-1} for valine chelate, for which the covalent character of the metal-nitrogen bond has been established.[2] Since the NH_2 stretching vibrations for the serine chelates are observed in the same region as those for valine chelates, the metal-nitrogen bonds of serine chelates must be fairly covalent and metal-nitrogen stretching vibrations for serine chelates should be in the region 400 to 360 cm^{-1}. Therefore the bands in this region of the chelates can be assigned to metal-nitrogen stretching vibration.

The carboxylate stretching vibrations are not shifted considerably on chelation, which indicates that the covalent character of metal-oxygen bond is weak. Consequently, metal-oxygen stretching vibration should be in the lower region than metal-nitrogen stretching vibration. Therefore the new bands at 217 cm^{-1} for platinum(II) chelate and 218 cm^{-1} for palladium(II) chelate can be assigned to metal-oxygen stretching vibration.

The skeletal deformation vibrations are assigned to the same range as those in the ligand by comparison with DL-α-leucine chelates.[3]

Copper Chelate. The spectra of the two species differ in many points as shown in Figs. 1 and 2. The principal difference is that the bands at 1250 and 686 cm^{-1} assigned to OH in plane and out-of-plane deformation vibrations respectively in copper(II) A chelate and in the ligand, disappear in copper(II) B chelate. In the far infrared region, the spectrum of B chelate is not similar to either those of A chelate or of any metal chelate. The copper(II) chelate studied by Nakamura[5] has no band to be assigned to OH deformation vibrations like the copper(II) B chelate. In addition, the X-ray spectra of copper(II) A chelate and copper (II) B chelate are different from each other. The infrared spectrum of the copper(II) chelate prepared from L-α-serine or D-α-serine does not coincide with either those of copper(II) A chelate or of copper(II) B chelate of DL-α-serine. It has been frequently discussed that the hydroxy group is coordinated with metal without changing its shape. The stability constants of metal-amino polycarboxylic acids chelates with hydroxy groups are higher than those without hydroxy groups. From this result it has been concluded that the hydroxy groups are coordinated to metals by forming chelate rings and that the chelates become stable.[10]

In the copper(II) B chelate, it may be assumed that the hydroxy group is coordinated with copper ion and becomes stable, since the basic character of the nitrogen atom of the amino group decreases from the inductive effect of the hydroxy group and since the copper ion can take on a distorted octahedral structure. Because the results of elementary analysis show the same values for both copper(II) A and copper(II) B chelates, it is doubtful whether the hydroxy group is coordinated to metal removing its hydrogen atom. In addition, it is hardly possible for the copper(II) B chelate to take the structure in which the hydroxy group forms a chelate ring, considering the bond distances and the bond angles of DL-α-serine studied by X-ray diffraction method.[11] Therefore copper(II) B chelate probably has the structure in which the hydroxy group bonds to another copper ion.

Thus, DL-α-serine chelates are found to be coordinated with metal through nitrogen and oxygen as well as other aliphatic α-amino acids, and the hydroxy group

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[10] T. Sakaguchi and K. Ueno, "Kinzoku Kireito," Vol. 1, Nanko-do, Tokyo (1965), p. 126.

[11] D. P. Shoemaker, R. E. Burieau, J. Donohue, and Chia-Si Lu, *Acta Crystallogr.*, **6**, 241 (1957).

TABLE 1. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR DL-α-SERINE AND METAL-DL-α-SERINE CHELATES (cm^{-1})

RH	PtR_2	PdR_2	CuR_2 A	CuR_2 B	NiR_2	Assignments
				3330 s		N-H str. and O-H str.
	3268 s	3285 s	3285 vs	3311 sh	3310 s	
	3203 m	3202 m		3244 s	3249 s	
	3097 s	3108 s	3139 s	3140 sh	3181 s	
2938 vs, b						
	2967 w	2961 w	2982 w		2980 w	C-H str.
	2950 w	2944 w	2930 w	2945 sh	2953 w	
	2919 w	2925 w		2929 w	2920 w	
	2891 w	2885 w	2870 w	2893 sh	2902 w	
					1713 m	H_2O
1662 vs						NH_3^+ deg. def.
1633 s						
1583 vs	1640 vs	1623 s	1621 vs	1628 s	1603 vs	COO^- asym. str.
	1598 m	1589 s	1589 vs	1583 s	1581 s	NH_2 scissors
1513 vs						NH_3^+ symm. def.
1506 vs						
1455 sh	1457 w	1458 w	1444 s		1481 s	CH_2 scissors
1435 s	1402 m	1404 s	1408 s	1397 s	1428 s	COO^- symm. str.
1377 w	1372 w	1377 w	1373 vw	1358 m	1372 s	CH_2 twisting
1355 vs	1331 w	1334 m	1359 m	1337 m		CH bending
1313 vs	1291 s	1287 s	1287 w	1288 m	1307 m	CH_2 wagging
1250 s	1242 s	1252 w	1250 w		1249 w	OH in plane def.
1186 m		1220 m	1206 w			
1166 m	1189 w	1172 m	1160 s	1153 s	1165 s	NH_2 wagging and CH bending for metal complexes NH_3^+ rocking for DL-α-serine
1154 m				1131 s		
	1102 m	1105 s	1108 s	1110 m	1108 s	NH_2 twisting
1098 s	1082 s	1080 m	1060 s	1057 sh	1062 s	C-N str.
				1040 s		
1030 vs	991 m	992 m	1000 s	1001 m	997 m	C-OH str.
988 m						
902 m	922 m	919 m	917 m	915 w	921 w	
851 w	874 w	868 m	890 w	885 w	867 w	C-C str.
			868 w			
			851 w			
830 w	850 m	831 m	831 m	829 vw	829 m	COO^- scissors and C-C str.
816 w			809 vw			
782 vw	776 w	756 m	786 w	784 m	762 m	CH_2 rocking
			731 w	728 m	701 vw	
729 m	698 m	687 m	686 w		667 m	OH out-of-plane def.
			651 m	647 m	652 m	NH_2 rocking
620 s	607 s	596 s	596 m	593 m	592 s	COO^- wagging
561 m	549 m	535 w	535 m	534 w	512 vw	COO^- rocking
526 m	521 w	513 w	519 m	494 vw	476 m	
503 m			438 w	434 m		
	404 w	407 m	373 m	394 vw	350 sh	M-N str.
375 mb		347 vw	347 w	348 m		
328 mb	335 vw	320 m	328 m	328 m		CCCN asym. def.
			319 m		317 sh	
	315 w	303 vw				
	284 w	283 m	285 w		293 m	CCCN symm. def.
225 mb	235 w	235 w	220 wb	230 m	240 w	CCCN def.
	217 w	218 w				MO str.

Abbreviations: RH=DL-α-serine, s=strong, m=medium, w=weak, sh=shoulder, b=broad probably does not participate in coordination except in the case of copper(II) B chelate.

Normal Coordinate Analysis. A normal coordinate analysis for a metal chelate was performed as a 27-body problem using the model illustrated in Fig. 3. The calculations were carried out on HITAC 5020E[12] and IBM 1130 computers.

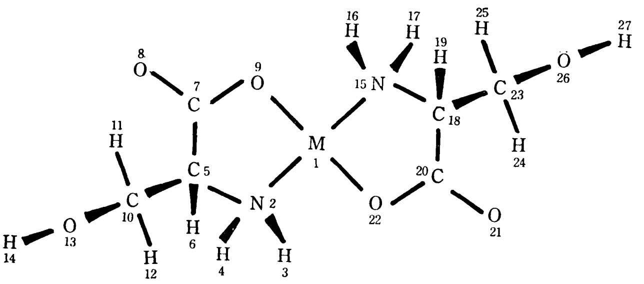

Fig. 3. Structure of DL-α-serine chelates.

The model adopted has M_1 as a center of symmetry. In the left side of the model, M_1, N_2, C_5, C_7, and O_9 form a planar five membered chelate ring and O_8 is on the same plane. The atoms C_5, C_{10}, O_{13}, and H_{14} are on the same plane which is perpendicular to this chelate ring and H_{11}, C_{10}, and H_{12} are on the same plane which is parallel to this chelate ring. Since no X-ray data for metal-DL-α-serine chelate is available, the bond lengths and bond angles listed in Table 2 were used in the calculation. They were taken from Refs. 4, 11, and 13.

Table 2. Bond lengths and bond angles used in the calculation for DL-α-serine chelate

Bond lengths (Å)					
1.	M_1–N_2	1.86	8.	O_9–M_1	1.916223
2.	N_2–H_3	1.01	9.	C_5–H_6	1.09
3.	N_2–H_4	1.01	10.	C_5–C_{10}	1.513
4.	N_2–C_5	1.491	11.	C_{10}–H_{11}	1.09
5.	C_5–C_7	1.528	12.	C_{10}–H_{12}	1.09
6.	C_7–O_8	1.261	13.	C_{10}–O_{13}	1.425
7.	C_7–O_9	1.252176	14.	O_{13}–H_{14}	0.956
Bond angles (°)					
O_9–M_1–N_2		90	O_8–C_7–O_9		120
C_5–C_7–O_8		120	C_7–O_9–M_1		$330-2\theta$
C_5–C_7–O_9		120			

θ: 190°28′

All other angles are assumed to be 109°28′. The same bond lengths and bond angles are used for second chelate ring.

The frequencies of infrared active species were calculated using the symmetry coordinates listed in Table 3. Wilson's *GF* matrix method[14] was used and all results were obtained using FORTRAN program designed by Shimanouchi.[15] The potential field employed was the following modified Uray-Bradley type,

$$2V = \sum_{i} \boldsymbol{K}_i(\Delta r_i)^2 + \sum_{i<j} \boldsymbol{H}_{ij}(r_0 \Delta\alpha_{ij})^2 + \sum_{i<j} \boldsymbol{F}_{ij}(\Delta q_{ij})^2 + \sum_{i<j} \boldsymbol{F}'_{ij}\mathbf{Y} + \boldsymbol{P}(\Delta\omega)^2 + \sum_{i<j} \boldsymbol{T}_{ij}(\Delta\tau_{ij})^2$$

$$\Delta q_{ij} = S_{ij}\Delta r_i + S_{ji}\Delta r_j + (t_{ij}t_{ji})^{1/2}(r_0\Delta\alpha_{ij})^2$$

$$\begin{aligned}\mathbf{Y} = {} & t_{ij}{}^2(\Delta r_i)^2 + t_{ji}{}^2(\Delta r_j)^2 - S_{ij}S_{ji}(r_0\Delta\alpha_{ij})^2 \\ & - 2t_{ij}t_{ji}(\Delta r_i)(\Delta r_j) + 2t_{ij}S_{ji}r_i(\Delta r_i)(\Delta\alpha_{ij}) \\ & + 2t_{ji}S_{ij}r_i(\Delta r_j)(\Delta\alpha_{ij})\end{aligned}$$

$$r_0 = (r_i r_j)^{1/2}, \quad S_{ij} = (r_i - r_j \cos\alpha_{ij})/q_{ij},$$

$$t_{ij} = r_j \sin\alpha_{ij}/q_{ij}$$

where r_i is a bond length and α_{ij} is the angle between bonds r_i and r_j at an equilibrium position. q_{ij} is the distance between atoms i and j which are bonded to a common atom. ω is the angle between the C–C-(ring) bond and the COO⁻ plane. τ_{ij} is the torsion about the axis connecting atoms i and j. These torsions are C–C(ring), C–C, and C–OH.

The force constants are given by $\boldsymbol{K}$(stretching), $\boldsymbol{H}$ (bending), $\boldsymbol{F}$(repusion), $\boldsymbol{P}$(out-of-plane wagging) and $\boldsymbol{T}$(torsion). $\boldsymbol{F}'$ is introduced as a force constant associated with the linear terms of the repulsion energy and remains in this equation as an internal tension. The value of $\boldsymbol{F}'$ is estimated to be $-0.1\boldsymbol{F}$. Table 4 shows the observed and calculated frequencies, poten-

Table 3. Symmetry coordinates of the infrared active species for DL-α-serine chelates

	Description of coordinate		Description of coordinate
S_1	OH str.	S_{23}	CH_2 rocking
S_2	NH_2 asym. str.	S_{24}	COO^- scissors
S_3	NH_2 sym. str.	S_{25}	MO bending
S_4	CH_2 asym. str.	S_{26}	COO^- rocking
S_5	CH_2 sym. str.	S_{27}	MN str.
S_6	CH str.	S_{28}	CCCN asym. def.
S_7	NH_2 scissors	S_{29}	CCCN asym. def.
S_8	CH_2 scissors	S_{30}	CCCN sym. def.
S_9	COO^- asym. str.	S_{31}	CCO def.
S_{10}	COO^- sym. str.	S_{32}	MO str.
S_{11}	CO str.	S_{33}	MNC def.
S_{12}	OH in plane def.	S_{34}	COM def.
S_{13}	NH_2 wagging	S_{35}	MN bending
S_{14}	CH_2 wagging	S_{36}	COO^- wagging
S_{15}	NH_2 twisting	S_{37}	COO^- twisting
S_{16}	CH_2 twisting	S_{38}	C-CH_2 torsion
S_{17}	CN str.	S_{39}	OH torsion
S_{18}	NC-COO^- str.	S_{40}	redundancy N
S_{19}	CH_2-CH str.	S_{41}	redundancy C_5
S_{20}	CH bending	S_{42}	redundancy C_{10}
S_{21}	CH bending	S_{43}	redundancy C_7
S_{22}	NH_2 rocking		

The contents of symmetry coordinates are the same as those of Ref. (4) except OH vibrations.

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[12] These calculations are performed at Computer Centre, The University of Tokyo.

[13] "Kagaku Binran Kiso hen II," Maruzen Inc., Tokyo (1966), p. 1163.

[14] E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[15] T. Shimanouchi, "Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules," The University of Tokyo, Tokyo (1968).

Table 4. Observed and calculated frequencies and potential energy distributions among symmetry coordinates and force constants for the infrared active vibrations of the platinum(II) chelate

Obsd cm^{-1}	Calcd cm^{-1}	PED in symmetry coordinates %	PED in force constants %	Description
3268	3259	S_2 (100)	$\boldsymbol{K}$(N–H) 96	NH_2 asym. str.
3203	3213	S_3 (100)	$\boldsymbol{K}$(N–H) 95	NH_2 symm. str.
3097	3103	S_1 (99)	$\boldsymbol{K}$(O–H) 94	OH str.
2967	2978	S_4 (100)	$\boldsymbol{K}$(C–H) 82, $\boldsymbol{F}$(HCO_{13}) 14	CH_2 asym. str.
2950	2948	S_5 (97)	$\boldsymbol{K}$(C–H) 79, $\boldsymbol{F}$(HCO_{13}) 16	CH_2 symm. str.
2919				
2891	2878	S_6 (101)	$\boldsymbol{K}$(C–H) 87	CH str.
1640	1641	S_9 (85), S_{26}(15)	$\boldsymbol{K}$(C–O_8) 55, $\boldsymbol{K}$(C–O_9) 28	COO^- asym. str.
1598	1600	S_7 (99)	$\boldsymbol{H}$(HNH) 81	NH_2 scissors
1457	1458	S_8 (47), S_{14}(41)	$\boldsymbol{F}$(HCO_{13}) 39, $\boldsymbol{H}$(HCH) 32	CH_2 scissors
1402	1408	S_{10}(93), S_{24}(28)	$\boldsymbol{K}$(C–O_9) 40, $\boldsymbol{K}$(C–O_8) 20	COO^- symm. str.
1372	1374	S_{16}(64), S_{12}(16)	$\boldsymbol{F}$(HCO_{13}) 47, $\boldsymbol{H}$(HCO_{13}) 18	CH_2 twisting
1331	1332	S_{21}(54), S_{20}(18)	$\boldsymbol{H}$(NCH) 36, $\boldsymbol{F}$(NCH) 21	CH bending
1291	1292	S_{14}(61), S_8 (55)	$\boldsymbol{H}$(HCH) 38, $\boldsymbol{H}$($C_{10}C_5H_6$) 26	CH_2 wagging
1242	1244	S_{12}(73), S_{16}(21)	$\boldsymbol{H}$($CO_{13}H$) 42, $\boldsymbol{F}$($CO_{13}H$) 29	OH in plane def.
1189	1193	S_{13}(44), S_{20}(39)	$\boldsymbol{H}$(MNH) 17, $\boldsymbol{H}$(HNC) 16	NH_2 wagging
	1148	S_{13}(52), S_{21}(25)	$\boldsymbol{H}$(MNH) 22, $\boldsymbol{H}$(HNC) 17	NH_2 wagging
1102	1116	S_{15}(77)	$\boldsymbol{H}$(HNC) 33, $\boldsymbol{F}$(HNC) 25	NH_2 twisting
1082	1069	S_{17}(48), S_{23}(12)	$\boldsymbol{K}$(N–C) 31, $\boldsymbol{F}$(NCH) 11	CN str.
991	995	S_{11}(45), S_{24}(17)	$\boldsymbol{K}$(C–OH) 20, $\boldsymbol{F}$(OCO) 14	CO str.
	978	S_{11}(52), S_{24}(26)	$\boldsymbol{K}$(C–OH) 22, $\boldsymbol{F}$(OCO) 20	CO str.
922				
874	893	S_{19}(37), S_{23}(29)	$\boldsymbol{F}$($C_{10}C_5H_6$) 20, $\boldsymbol{K}$(C_5–C_{10}) 16	CC str.
850	835	S_{23}(18), S_{19}(18)	$\boldsymbol{F}$($C_5C_{10}O_{13}$) 18, $\boldsymbol{F}$($C_{10}C_5H_6$) 15	CC str.
776	768	S_{23}(37), S_{22}(13)	$\boldsymbol{H}$($C_{10}C_5H_6$) 18, $\boldsymbol{F}$($C_{10}C_5H_6$) 13	CH_2 rocking
698	698	S_{39}(100)	$\boldsymbol{T}$(C_{10}–O_{13}) 100	OH out of plane def.
	688	S_{22}(67), S_{19}(10)	$\boldsymbol{H}$(MNH) 33, $\boldsymbol{H}$(HNC) 15	NH_2 rocking
607	607	S_{36}(100),	$\boldsymbol{P}$($O_8C_7O_9$) 100	COO^- wagging
	592	S_{31}(38), S_{18}(20)	$\boldsymbol{H}$($C_5C_{10}O_{13}$) 17, $\boldsymbol{F}$(CCO_9) 14	CCO def.
549	533	S_{26}(42), S_{17}(18)	$\boldsymbol{F}$(CCO_8) 20, $\boldsymbol{H}$(CCO_8) 18	COO^- rocking
521				
404	406	S_{27}(54), S_{28}(17)	$\boldsymbol{K}$(M–N) 40, $\boldsymbol{F}$(MNH) 11	MN str.
335	323	S_{29}(41), S_{31}(9)	$\boldsymbol{H}$($C_7C_5C_{10}$) 44, $\boldsymbol{F}$($C_7C_5C_{10}$) 19	CCCN asym. def.
315				
284	265	S_{30}(45), S_{29}(15)	$\boldsymbol{H}$(NC_5C_{10}) 15, $\boldsymbol{F}$(NC_5C_{10}) 7	CCCN symm. def.
235				
217	217	S_{32}(35), S_{28}(23)	$\boldsymbol{H}$(NC_5C_{10}) 22, $\boldsymbol{K}$(O–M) 27	OM str.

tial energy distributions to symmetry coordinates and force constants with an approximate description of the vibrational mode for the platinum(II) chelate. The force constants used in this calculation are listed in Table 5. They were evaluated so as to obtain the best fit between the calculated and the observed frequencies by a trial and error method guided by the values of a Jacobian matrix.

Metal-ligand Bonds. A similar calculation was accomplished for the palladium(II), copper(II) A, and nickel(II) chelates and good agreement was obtained between the observed and calculated frequencies for these chelates as well as for those of the platinum(II) chelate. In Table 6 the important frequencies related to the metal-ligand bonds are summarized for each chelate. The force constants used in these calculations are given in Table 7.

As seen in Table 6, the frequency separation of COO^- antisymmetric and symmetric stretching vibrations increases from the nickel(II) chelate to the platinum (II) chelate except for the copper(II) B chelate. The values of $\boldsymbol{F}_{\mathrm{dia}}$(M–O) and $\boldsymbol{K}$(M–O) for platinum(II) chelate are larger than those of palladium(II) chelate as seen in Table 7. Therefore, the covalent character of the metal-oxygen bond can be considered to increase in the order Ni(II)<Cu(II)<Pd(II)<Pt(II). This same order has already been reported for glycine,[1] alanine,[4] and other aliphatic α-amino acids chelates.[2,3] A similar trend is observed in the COO^- rocking vibration. Although the metal-nitrogen stretching frequencies increase in the order Ni(II)< Cu(II)<Pt(II)<Pd(II), the force constants of the metal-nitrogen stretching vibration and the frequencies of the NH_2 scissors increase in the order Ni(II)<

TABLE 5. FORCE CONSTANTS USED IN THE CALCULATION FOR THE PLATINUM(II) CHELATE (mdyn/Å)

Streching		Bending		Repulsion	
K(M-N)	0.75	**H**(MNH)	0.19	**F**(MNH)	0.09
K(N-H)	5.55	**H**(MNC)	0.05	**F**(MNC)	0.10
K(N-C)	2.50	**H**(HNH)	0.57	**F**(HNH)	0.06
K(C_5-C_7)	1.50	**H**(HNC)	0.20	**F**(HNC)	0.40
K(C-O_8)	7.90	**H**(NCH)	0.285	**F**(NCH)	0.54
K(C-O_9)	6.80	**H**(NC_5C_7)	0.20	**F**(NC_5C_7)	0.20
K(O-M)	0.42	**H**(NC_5C_{10})	0.20	**F**(NC_5C_{10})	0.20
K(C-H)	3.96	**H**($C_7C_5H_6$)	0.19	**F**($C_7C_5H_6$)	0.36
K(C_5-C_{10})	1.50	**H**($C_7C_5C_{10}$)	0.40	**F**($C_7C_5C_{10}$)	0.30
K(C-O_{13})	2.30	**H**($H_6C_5C_{10}$)	0.187	**F**($H_6C_5C_{10}$)	0.36
K(O-H)	5.13	**H**(CCO_8)	0.50	**F**(CCO_8)	0.70
		H(CCO_9)	0.50	**F**(CCO_9)	0.70
		H(OCO)	0.65	**F**(OCO)	2.50
		H(COM)	0.05	**F**(COM)	0.10
		H(OMN)	0.05	**F**(OMN)	0.05
		H($C_5C_{10}O_{13}$)	0.45	**F**($C_5C_{10}O_{13}$)	1.20
		H(HCH)	0.37	**F**(HCH)	0.05
		H(HCO_{13})	0.16	**F**(HCO_{13})	1.288
		H($CO_{13}H$)	0.325	**F**($CO_{13}H$)	0.598
		H($O_{22}MN$)	0.05	**F**($O_{22}MN$)	0.05

Out-of-plane wagging **P**(COO^-) 0.54 mdyn·Å

Torsion **T**(C_5-C_7) 0.15 mdyn·Å, **T**(C_5-C_{10}) 0.065 mdyn·Å, **T**(C_{10}-O_{13}) 0.194 mdyn·Å

TABLE 6. OBSERVED AND CALCULATED FREQUENCIES RELATED TO THE METAL-LIGAND BOND (cm^{-1})

Vib. Mode	Pt(II)		Pd(II)		Cu(II) A		Cu(II) B		Ni(II)	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
NH_2 asym. str.	3268	3259	3285	3260	3285	3286	3311		3310	3294
NH_2 symm. str.	3203	3213	3202	3217		3239	3244		3249	3246
COO^- asym. str.	1640	1641	1623	1627	1621	1621	1628		1603	1606
NH_2 scissors	1598	1600	1589	1590	1589	1577	1583		1581	1580
COO^- symm. str.	1402	1408	1404	1388	1408	1408	1397		1428	1421
OH in plane def.	1242	1244	1252	1254	1250	1249			1249	1248
NH_2 wagging	1189	1193	1172	1178	1160	1168	1153		1165	1165
OH out of plane def.	698	698	687	688	686	686			667	665
COO^- wagging	607	607	596	595	596	596	593		592	592
COO^- rocking	549	533	535	524	535	524	534		512	515
MN str.	404	406	407	410	373	374	394		350	351
MO str.	217	217	218	222						

TABLE 7. VALUES OF FORCE CONSTANTS AND F_{dia} RELATED TO THE METAL-LIGAND BONDS

Force constant (mydn/Å)	Pt(II)	Pd(II)	Cu(II)A	Ni(II)	Force constant	Pt(II)	Pd(II)	Cu(II)A	Ni(II)
K(MN)	0.75	0.70	0.40	0.22	**T**(CO) mdyn·Å	0.19	0.19	0.19	0.18
K(NH)	5.55	5.55	5.65	5.68	**P**(OCO) mdyn·Å	0.54	0.52	0.52	0.52
K(CO_{ring})	6.80	6.80	6.80	6.70	F_{dia}(NH_2 asym. str.) mdyn/Å	5.78	5.78	5.87	5.90
K(CO)	2.30	2.40	2.44	2.50					
K(OH)	5.13	5.17	5.26	5.45	F_{dia}(COO^- asym. str.) mdyn/Å	7.72	7.67	7.62	7.52
K(MO)	0.42	0.35							
H(HNH)	0.57	0.56	0.56	0.56	F_{dia}(MN str.) mdyn/Å	1.01	0.98	0.65	0.45
H(CCO_{ring})	0.50	0.45	0.45	0.40	F_{dia}(MO str.) mdyn/Å	0.55	0.48		
H(OCO)	0.65	0.50	0.71	0.55	F_{dia}(NH_2 rocking) mdyn·Å	0.47	0.46	0.43	0.43
H(COH)	0.33	0.34	0.34	0.33	F_{dia}(CO torsion) mdyn·Å	0.19	0.19	0.19	0.18
H(MNH)	0.19	0.17	0.15	0.15					

F_{dia} = the diagonal elements of the symmetrized **F** matrix

Cu(II) < Pd(II) < Pt(II). The frequencies of the NH_2 wagging vibration show a slightly different trend. This fact can be explained by considering how little the metals affect this vibration, since the NH_2 wagging vibration is closely coupled with other vibrations as seen in Table 4. The calculated frequency of metal-nitrogen stretching vibration agrees fairly well with the observed frequency, and the force constant takes a reasonable value for each chelate. Therefore, considering the value of $\boldsymbol{K}$(M–N) and $\boldsymbol{F}_{\mathrm{dia}}$(M–N), it is reasonable to conclude that the strength of the metal-nitrogen bond increases in the order Ni(II) < Cu(II) < Pd(II) < Pt(II). This trend is the same as that in many aliphatic α-amino acids chelates.[1–4] From these facts it might be asserted that the hydroxy group in the β-position of DL-α-serine has no influence on the order of the metal-ligand bond strength, which has been already found in aliphatic α-amino acid chelates having no hydroxy group in the β-position.