

## Infrared Absorption Spectra and Normal Coordinate Analysis of Metal-DL-Tyrosine Chelates

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The infrared absorption spectra of DL-tyrosine and six metal DL-tyrosine chelates have been investigated from 4000 to 300  $\text{cm}^{-1}$ . A detailed normal coordinate analysis was performed for the metal chelates as a 39-body problem and an approximate description of the vibrational modes has been assigned to the observed frequencies. DL-Tyrosine chelates are found to be coordinated with the metal through nitrogen and oxygen and to have a *trans* configuration; the same is true for other aliphatic amino acid chelates. The bond-stretching force constants for the metal-nitrogen bonds have been found to decrease in the order  $\text{Pd(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Ni(II)} > \text{Co(II)}$ . The calculated frequencies, which were obtained using the same force constants as in other aliphatic amino acid chelates, were in good agreement with the observed frequencies.

The infrared absorption spectra and the normal coordinate analysis for aliphatic  $\alpha$ -amino acid chelates have already been studied.<sup>1-4)</sup> However, amino acids having a substituent in the  $\beta$ -position and their metal-chelates have not yet been studied in detail. Recently, the authors have investigated the infrared spectra and the normal coordinate analysis for DL- $\alpha$ -serine<sup>5)</sup> having a hydroxy group and DL-phenylalanine<sup>6)</sup> having a benzene ring in the  $\beta$ -position.

Laurie<sup>7)</sup> has synthesized three isomers of bis(DL-tyrosino)-copper(II) and reported that two isomers have a *trans* configuration, and the third is 4-coordinated with either a *trans* or *cis* configuration. He used both diffuse reflectance spectra and infrared absorption spectra for this configuration assignment.

In the present investigation, detailed assignments for the infrared absorption bands of DL-tyrosine and its six metal chelates have been made by a comparison with the results of the normal coordinate analysis. In addition, we discuss how the phenolic group in the  $\beta$ -position influences the order of the metal-ligand bond strength which has already been found in aliphatic  $\alpha$ -amino acid chelates.<sup>8)</sup>

### Experimental

**Preparation of Compounds.** Bis(DL-tyrosino)-palladium(II) was prepared by adding 0.81 g (0.0025 mol) of  $\text{K}_2\text{PdCl}_4$  to hot water in which 0.91 g (0.005 mol) of DL-tyrosine was thoroughly dissolved, and stirring for half an hour. The yellow crystals which precipitated were washed with hot water and dried at room temperature *in vacuo* for several hours.

Found: C, 45.75; H, 4.22; N, 5.98% Calcd for  $\text{Pd}[\text{C}_6\text{H}_4\text{OHCH}_2\text{CHNH}_2\text{CO}_2]_2$ : C, 46.31; H, 4.33; N, 6.00%

Bis(DL-tyrosino)-copper(II) was prepared by the method of Laurie,<sup>7)</sup> which yielded the blue, prismatic form of bis(DL-tyrosino)-copper(II).

Found: C, 45.95; H, 5.47; N, 5.90% Calcd for  $\text{Cu}[\text{C}_6\text{H}_4\text{OHCH}_2\text{CHNH}_2\text{CO}_2]_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ : C, 46.09; H, 5.38; N, 5.97%.

Bis(DL-tyrosino)-nickel(II) was prepared by adding 1.2 g (0.005 mol) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  to a hot solution of 1.81 g (0.01 mol) of DL-tyrosine and 0.56 g (0.01 mol) of KOH and stirring. After filtering while hot, the filtrate was allowed to stand overnight. The sky blue precipitate separated was recrystallized from hot water and dried at room temperature *in vacuo* for several hours.

Found: C, 45.91; H, 5.41; N, 5.93% Calcd for  $\text{Ni}[\text{C}_6\text{H}_4\text{OHCH}_2\text{CHNH}_2\text{CO}_2]_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ : C, 46.57; H, 5.44; N, 6.04%.

Bis(DL-tyrosino)-cobalt(II)

Found: C, 48.99; H, 5.10; N, 6.35% Calcd for  $\text{Co}[\text{C}_6\text{H}_4\text{OHCH}_2\text{CHNH}_2\text{CO}_2]_2 \cdot 1\frac{1}{3}\text{H}_2\text{O}$ : C, 48.43; H, 5.20; N, 6.28%.

Bis(DL-tyrosino)-cadmium(II)

Found: C, 44.90; H, 4.20; N, 5.74% Calcd for  $\text{Cd}[\text{C}_6\text{H}_4\text{OHCH}_2\text{CHNH}_2\text{CO}_2]_2$ : C, 45.72; H, 4.27; N, 5.93%.

Bis(DL-tyrosino)-zinc(II)

Found: C, 45.61; H, 5.08; N, 5.86% Calcd for  $\text{Zn}[\text{C}_6\text{H}_4\text{OHCH}_2\text{CHNH}_2\text{CO}_2]_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ : C, 45.92; H, 5.36; N, 5.95%.

These three chelates were prepared by employing essentially the same procedure as for the nickel(II) chelate. For cobalt(II) chelate, after filtering the solution while it was hot, the pink filtrate was allowed to stand for several days at room temperature. The precipitates of cobalt(II), cadmium(II), and zinc(II) chelates were washed twice in hot water and dried at room temperature *in vacuo*.

**Deuteration of Compounds.** The deuterated DL-tyrosine and copper(II) chelate were prepared by dissolving DL-tyrosine and copper(II) chelate, which had been dried thoroughly, in 99.75% deuterium oxide at 80°C and drying them *in vacuo*. The NH and OH groups were deuterated by this method. The perfect deuteration of the other chelates was difficult, since they were insoluble in water.

**Thermal Analysis of Chelates.** Thermal analysis was carried out with a Rigaku Denki TG-DTA from room temperature 250°C in air; the decrease in weight was measured when an endothermic reaction occurred. It was found that the nickel(II), the copper(II), and the zinc(II) chelates had  $2\frac{1}{2}$  molecules of water and cobalt(II) had  $1\frac{1}{2}$  molecules. The cadmium(II) and the palladium(II) chelates had no water.

**Absorption Measurement.** Infrared absorption spectra from 4000  $\text{cm}^{-1}$  to 300  $\text{cm}^{-1}$  were obtained with Hitachi EPI-G2 and EPI-L spectrophotometers, which were calibrated with polystyrene and atmospheric water vapor. Samples were prepared as potassium bromide discs and nujol mulls. The observed absorption frequencies and assignments for DL-tyrosine and the metal chelates are listed in Table 1.

### Discussion

The assignments for DL-tyrosine and its metal chelates have been based on a comparison of the observed spectra with those of aliphatic  $\alpha$ -amino acids,<sup>1-5)</sup> DL-phenylalanine,<sup>6)</sup> and those metal chelates which had

TABLE 1. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR DL-TYROSINE AND METAL-DL-TYROSINE CHELATES ( $\text{cm}^{-1}$ )

RH	Pd(II)	Cu(II)	Ni(II)	Zn(II)	Co(II)	Cd(II)	Assignments
			3599 m	3519 m	3399 sb		OH str. (water of crystallization)
			3359 vs	3348 s		3345 s	
	3294 sb	3307 sb	3302 vs	3328 s	3277 sb	3331 s	NH str. for chelates
3212 s	3239 s	3255 sb		3267 s	3244 sb	3283 s	OH str.
	3159 sh					3272 sh	
	3125 sh	3144 sb		3187 sb	3159 sb	3109 wb	
3117 s						3069 w	
3046 s						3037 m	NH <sub>3</sub> <sup>+</sup> str. for the ligand
3029 s	3029 w	3016 m	3029 m	3015 w	3026 w	3019 m	CH str. of benzene ring
2971 s	2976 vw	2959 w		2959 m	2969 sh	2952 m	
	2951 w			2936 m	2959 sh		
2943 s	2919 w	2931 sh	2937 m	2917 w	2935 w	2915 m	CH str. of CH <sub>2</sub> and CH
2882 sh							
	2849 w	2853 sh	2860 w	2858 w	2855 sh	2846 m	
2827 s	2784 sh	2806 m		2813 wb	2819 w	2819 m	
2747 s			2760 sh	2736 w		2758 w	
	2694 sh	2689 w		2679 w	2694 sh	2694 mb	NH <sub>3</sub> <sup>+</sup> str. for the ligand
2652 s							
2601 s		2608 w	2628 sh	2604 w	2612 w	2624 m	
2501 m		2512 w		2514 vw		2517 w	
2094 m							
		1652 sh					
		1647 sh	1648 sh		1654 sh		
		1633 sh	1632 sh		1648 sh		
1627 s	1636 sb	1630 s	1625 s		1636 s		COO <sup>-</sup> asym. str. + C=C str.
1608 s		1607 s		1597 vs	1629 s	1608 m	NH <sub>3</sub> <sup>+</sup> deg. def. + C=C str. for ligand
	1584 s	1591 s	1592 s	1570 sh	1610 sh	1584 s	
1588 s							NH <sub>2</sub> scissors + C=C str.
1528 s						1548 s	COO <sup>-</sup> asym. str. + C=C str. for ligand
1510 s	1503 m	1507 m	1512 m	1511 s	1510 m	1512 s	C=C str.
1448 m			1458 m	1468 vw	1457 sh	1458 sh	
				1458 sh		1450 w	
1434 m	1433 m	1437 m	1447 sh	1445 m	1445 m	1435 m	C=C str. + CH <sub>2</sub> scissors
				1411 s	1439 m	1412 m	
						1382 sh	
1410 m	1357 s	1373 s	1391 s	1357 m	1378 s	1357 m	COO <sup>-</sup> sym. str. + CH bending (metal chelates)
1367 s		1341 m		1349 sh			
1330 s	1321 vw	1330 m	1336 m	1331 w	1330 m	1341 m	CH bending + C=C str.
	1306 vw	1304 sh	1308 sh	1307 vw	1307 sh	1315 w	CH <sub>2</sub> wagging
1289 w	1290 m						CH in plane deformation of benzene ring
							CH <sub>2</sub> twisting
1269 w							C-O str.
1249 s	1261 m	1265 m		1255 s	1264 sh	1255 m	OH in plane def.
1216 m	1205 s	1235 m	1247 s	1242 m	1237 s	1231 w	NH <sub>3</sub> <sup>+</sup> rocking
1199 m							
				1212 w		1215 m	
1180 m	1171 vw	1167 w	1171 w	1172 vw	1184 vw	1178 m	CH in plane deformation of benzene ring
					1172 vw		CCN asym. str.
1150 m	1151 sh		1139 w	1146 w		1141 w	
	1137 s						
1113 m		1105 m	1099 m	1115 m	1102 w	1113 m	CH in plane deformation of benzene ring
	1097 w			1100 s			
	1084 w	1085 m		1081 s	1093 sh	1077 m	NH <sub>2</sub> wagging
1098 m							NH <sub>3</sub> <sup>+</sup> rocking

Table 1. (continued)

RH	Pd(II)	Cu(II)	Ni(II)	Zn(II)	Co(II)	Cd(II)	Assignments
1047 m	1062 sh		1057 s			1047 w	CH <sub>2</sub> -C str.
1018 w	1021 vw 1011 vw	1010 sh	1013 vw	1020 vw	1010 w	1013 w	CH in plane deformation of benzene ring
989 w							
985 w	976 vw 963 vw 947 vw	989 w	985 w	978 m		986 m 952 vw	C=C def.
938 w	932 w	932 wb	924 w	936 w	945 wb	926 vw	CH out of plane deformation of benzene ring
897 w	919 sh					903 w 897 m	
876 m	860 w	864 w	868 w	871 vw	864 sh	871 m	CCN sym. str.
842 s			850 sh	851 vw	851 sh		
	837 sh			831 sh		831 m	C-C str.
834 m	822 s	824 m	821 s	820 m	816 m	817 m	CH out of plane deformation of benzene ring
808 m	805 m	810 m	811 s	806 m		810 m	COO <sup>-</sup> scissors
797 m	782 w			775 vw		773 vw	CH <sub>2</sub> rocking
738 m	724 w	730 w	741 w	727 m	744 sh	735 m	
711 w	707 vw	714 sh	719 w	707 w	713 wb	715 m	C=C out of plane deformation
			683 w				
644 m	668 sh 660 w	650 m	650 vw	665 m	658 w	672 w 658 vw	OH out of plane deformation
639 m	641 vw 622 vw 613 w		639 vw	640 vw	638 w	638 vw 621 sh	in plane benzene ring deformation
	583 w		587 m	603 w	582 m	599 m	NH <sub>2</sub> rocking
575 s			577 sh	590 vw		572 sh	COO <sup>-</sup> wagging
559 vw							
534 s	542 m	553 sh	532 m	534 m	543 m	539 m	CCC def.
	524 w	539 m	512 sh	523 w	533 m	520 vw	C=C def.
498 m	486 w	486 w	494 w	498 w	487 m	496 w	COO <sup>-</sup> rocking
478 vw				484 vw		484 w	
452 vw	443 vw			458 vw	447 m	463 w	
434 m	432 w 429 w	408 w	411 wb	410 w	423 w	439 w	C=C out of plane deformation
					400 w		
	407 m						M-N str.
385 s	392 m	393 w	381 wb	376 vw	385 sh	390 vw	CCO def.
	377 sh	372 vw	377 sh	370 vw	375 sh	370 vw	CCCN sym. def.
337 m	342 m				341 vw	352 w	CO out of plane def.
325 m		320 mb 317 mb	317 m	359 w	315 w	316 w	M-N str. for the chelates
308 m	305 w	305 w	305 vw		302 vw		

Abbreviations: RH=DL-tyrosine, s=strong, m=medium, w=weak, sh=shoulder, b=broad

been thoroughly studied.

The spectra of DL-tyrosine chelates are similar to the spectra of those which have a *trans* configuration. Laurie<sup>7)</sup> reported that the blue prismatic DL-tyrosine copper(II) chelate had a *trans* configuration. Therefore, in spite of the lack of X-ray data for the metal chelates, it seems reasonable that they have a *trans* configuration.

*Assignment of Observed Frequencies.* DL-Tyrosine: The sharp band at 3212 cm<sup>-1</sup> is assigned to the OH stretching vibration, because of its disappearance on deuteration and the absence of bands in this region

for DL-phenylalanine.<sup>6)</sup> The broad bands from 3100 to 2800 cm<sup>-1</sup> are due to NH<sub>3</sub><sup>+</sup> and CH stretching vibrations of the benzene ring. The CH stretching vibration bands are assigned easily, since they do not shift on deuteration. The CH stretching vibrations of an aliphatic group are observed in a lower frequency region than those of a benzene ring.

The bands at 1627, 1528, 1199, and 1098 cm<sup>-1</sup> which shift on deuteration are due to NH<sub>3</sub><sup>+</sup> deformation vibrations, since no corresponding bands appear in the metal chelates.

It is very difficult to assign C-O stretching and OH

deformation vibrations in the phenolic group. Jakobson<sup>9</sup>) has reported about the group frequencies of *para*-substituted phenols in detail. He shows that *p*-cresol has bands at 1253, 1215, 1170, and 555  $\text{cm}^{-1}$ , which have been assigned to C-O and C-CH<sub>3</sub> stretching and OH deformation vibrations. The frequencies of DL-tyrosine, however, may be different from those of *p*-cresol on account of the intermolecular hydrogen bonding. Therefore it is reasonable to assign the bands at 1249 and 1216  $\text{cm}^{-1}$  to the C-O stretching and the OH in plane deformation vibrations, and the band at 644  $\text{cm}^{-1}$  to the OH out of plane deformation vibration by a comparison with the *N*-deuterated compound and with phenylalanine.<sup>6)</sup>

CN and CC stretching and skeletal deformation vibrations are assigned by a comparison with the spectra of the metal chelates.

If the phenolic group (C<sub>6</sub>H<sub>4</sub>OH) is treated as possessing C<sub>2v</sub> symmetry, it has thirty normal vibrations which are divided into symmetry classes as follows: (11A<sub>1</sub>+10B<sub>1</sub>) planar and (3A<sub>2</sub>+6B<sub>2</sub>) non planar. The A<sub>2</sub> symmetry class is infrared inactive. The eight vibrations (4A<sub>1</sub>+3B<sub>1</sub>+B<sub>2</sub>) of these normal vibrations have already been mentioned above. The remaining 19 vibrations are assigned by referring to the assignments in *p*-cresol and phenylalanine.<sup>6)</sup>

**Metal-Chelates:** As the bands above 3500  $\text{cm}^{-1}$  of the nickel(II) and the zinc(II) chelates disappear in the spectra are obtained after DTA analyses, these bands are assigned to the OH stretching vibrations in the water of crystallization.

Although the bands from 3400 to 3100  $\text{cm}^{-1}$  are due to NH<sub>2</sub> symmetric and antisymmetric and OH stretching vibrations, it is difficult to assign them separately, since all bands shift on deuteration. The CH stretching vibrations are observed at the same region as in the ligand.

In the region 1700 to 500  $\text{cm}^{-1}$  the assignment of the observed bands is accomplished by a comparison of the spectrum of each chelate with that of the ligand.

For the metal chelates, the NH<sub>2</sub> deformation vibrations appear instead of NH<sub>3</sub><sup>+</sup> deformation vibrations of the ligand. The COO<sup>-</sup> antisymmetric stretching vibrations for all chelates are intense and overlap with the C=C stretching vibrations of the benzene ring and the NH<sub>2</sub> scissors vibrations to some extent. The COO<sup>-</sup> antisymmetric stretching vibrations are observed at higher frequencies and symmetric stretching vibrations are at lower frequencies than those of the ligand. The OH in plane and out of plane deformation vibrations shift to higher frequencies. The vibrations of the phenolic group and the skeletal deformation vibrations occur at the same regions as in the ligand.

From 500 to 300  $\text{cm}^{-1}$ , absorption bands which cannot be observed in the ligand appear at 407  $\text{cm}^{-1}$  for palladium(II) chelate, 393  $\text{cm}^{-1}$  for copper(II) chelate, 359  $\text{cm}^{-1}$  for zinc(II) chelate, 317  $\text{cm}^{-1}$  for nickel(II) chelate, 316  $\text{cm}^{-1}$  for cadmium(II) chelate and 315  $\text{cm}^{-1}$  for cobalt(II) chelate. They are assigned to the metal-nitrogen stretching vibration by comparison of chelate spectra with the ligand spectrum and by referring to the metal chelates of DL-

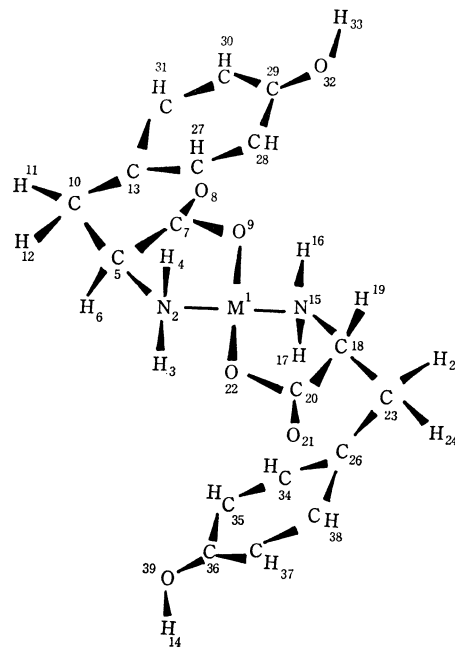


Fig. 1. Structure of DL-tyrosine chelates.

phenylalanine,<sup>6)</sup> DL-serine<sup>5)</sup> and other amino acids.<sup>1-4)</sup>

**Normal Coordinate Analysis.** The normal coordinate analysis for a metal chelate was performed as a 39-body problem using the model illustrated in Fig. 1. Major calculations were carried out on HITAC 5020E and 8700/8800 computers.<sup>10)</sup>

The model adopted has M<sub>1</sub> as a center of symmetry. The atoms M, N(2,15), C(5,18), C(7,20), O(9,22) form planar five-membered chelate rings and O(8,21) is in the same plane. The atoms C(5,18), C(10,25), C(13,26), C(29,36), and O(32,39) are in the same plane, which is perpendicular to these chelate rings. The atoms C(10,23) and phenolic groups are in the same plane, which makes half of a tetrahedral angle with

TABLE 2. BOND LENGTHS AND BOND ANGLES USED IN THE CALCULATION FOR DL-TYROSINE CHELATE

Bond lengths (Å)			
M-N	1.86 <sup>5)</sup>	C-H	1.09
N-H	1.01	C <sub>5</sub> -C <sub>10</sub>	1.55
N-C	1.48	C <sub>10</sub> -C <sub>13</sub>	1.57
C <sub>5</sub> -C <sub>7</sub>	1.50	C=C	1.37
C <sub>7</sub> -O <sub>8</sub>	1.25	C <sub>29</sub> -O <sub>32</sub>	1.43 <sup>12)</sup>
C <sub>7</sub> -O <sub>9</sub>	1.271583 <sup>a)</sup>	O-H	0.960 <sup>13)</sup>
O-M	1.881279 <sup>a)</sup>		
Bond angles (°)			
O <sub>9</sub> -M <sub>1</sub> -N <sub>2</sub>	90	O <sub>8</sub> -C <sub>7</sub> -O <sub>9</sub>	120
C <sub>5</sub> -C <sub>7</sub> -O <sub>8</sub>	120	C <sub>7</sub> -O <sub>9</sub> -M <sub>1</sub>	330-2θ
C <sub>5</sub> -C <sub>7</sub> -O <sub>9</sub>	120	C <sub>29</sub> -O <sub>32</sub> -H <sub>33</sub>	109 <sup>14)</sup>
C-C=C	120		
θ : 109°28'			

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

a) Calculated to insure ring closure.

these chelate rings.

The CH groups in the phenolic groups are considered as one unit. (Mass=13.007825)

In the absence of X-ray data, the bond lengths and bond angles listed in Table 2 were used for all DL-tyrosine metal chelates in the calculation.

The frequencies for the infrared active vibrations were calculated using the same symmetry coordinates as those of Ref. 4 except for the phenolic group vibrations.

Wilson's GF matrix method was used and all results were obtained using FORTRAN program designed by Shimanouchi.<sup>15)</sup> The potential field employed was the modified Uray-Bradley type, similar to that used for the chelates of DL- $\alpha$ -serine.<sup>5)</sup>

Most of the force constants in Table 3 were transferred from the corresponding values determined for the DL- $\alpha$ -serine<sup>5)</sup> and other amino acids chelates. The remaining force constants were evaluated so as to obtain the best fit between the calculated and observed frequencies. Adjustment of the force constant values was accomplished by a trial and error method guided by the values of a Jacobian matrix.

Calculated frequencies for the palladium(II) chelate are shown in Table 4. An approximate description

of the vibrational mode is given for each observed frequency, which is based on the potential energy distribution to the symmetry coordinates and force constants. In this model, the CH groups in the phenolic groups were considered as a single unit. Therefore, the frequencies corresponding to the stretching and deformation vibrations of those groups will not appear in the calculations.

A similar calculation was accomplished for the cadmium(II), copper(II), zinc(II), nickel(II) and cobalt(II) chelates and good agreement was obtained between the observed and calculated frequencies for these chelates.

**Metal-ligand Bonds.** The important frequencies and the force constants related to the metal-ligand bonds are summarized for each chelates in Table 5 and 6.

As shown in Table 5, the frequency separation of the COO<sup>-</sup> antisymmetric and symmetric stretching vibrations of chelates which have the same number of molecules of water increases in the order Ni(II) < Zn(II) < Cu(II). This trend is the same as that in many aliphatic  $\alpha$ -amino acid chelates.<sup>1-4,8)</sup>

In Table 6, the  $F_{dia}$  terms represent the diagonal elements of the symmetrized  $F$  matrix: *i. e.*, the

TABLE 3. FORCE CONSTANTS USED IN THE CALCULATION FOR THE PALLADIUM(II) CHELATE (mdyn/Å)

Stretching		Bending		Repulsion	
$K(M-N)$	0.75	$H(MNH)$	0.15	$F(MHN)$	0.07
$K(N-H)$	5.68	$H(MNC)$	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	$H(HNC)$	0.17	$F(HNC)$	0.40
$K(C_7-O_8)$	8.30	$H(NCH)$	0.26	$F(NCH)$	0.54
$K(C_7-O_9)$	5.60	$H(NCC_R)$	0.20	$F(NCC_R)$	0.20
$K(C_5-H_6)$	4.13	$H(NCC)$	0.20	$F(NCC)$	0.20
$K(C_5-C_{10})$	1.50	$H(HCC_R)$	0.23	$F(HCC_R)$	0.43
$K(C-H)$	4.13	$H(CCC)$	0.40	$F(CCC)$	0.30
$K(C-C_{13})$	1.50	$H(HCC)$	0.23	$F(HCC)$	0.43
$K(O-H_{33})$	5.27	$H(CCO)$	0.40	$F(CCO)$	0.70
$K(C_{13}-C_{27})$	6.25	$H(CCO_R)$	0.50	$F(CCO_R)$	0.70
$K(C_{27}-C_{28})$	6.25	$H(OCO)$	0.35	$F(OCO)$	3.50
$K(C_{28}-C_{29})$	6.25	$H(COM)$	0.05	$F(COM)$	0.10
$K(C_{29}-O_{32})$	2.50	$H(CCH)$	0.23	$F(CCH)$	0.43
		$H(CCC_B)$	0.40	$F(CCC_B)$	0.37
		$H(HCH)$	0.42	$F(HCH)$	0.05
		$H(HCC_B)$	0.23	$F(HCC_B)$	0.43
		$H(CC_B C_B)$	0.23	$F(CC_B C_B)$	0.37
		$H(C_B C_B C_B)$	0.33	$F(C_B C_B C_B)$	0.27
		$H(C_B C_O C_B)$	0.23	$F(C_B C_O C_B)$	0.37
		$H(C_B C_{13} C_B)$	0.23	$F(C_B C_{13} C_B)$	0.37
		$H(CC_B O)$	0.23	$F(CC_B O)$	0.37
		$H(C_B OH)$	0.30	$F(C_B OH)$	0.67
Out-of-plane wagging		mdyn·Å			
$P(C_{13}-C)$	0.18	$P(C_{29}-O)$	0.08	$P(OCO)$	0.50
Torsion		mdyn·Å			
$T(C_{13}-C_{27})$	0.15	$T(C_{10}-C_{13})$	0.15	$T(C_{27}-C_{28})$	0.15
$T(C_5-C_7)$	0.15	$T(C_{28}-C_{29})$	0.15	$T(C_5-C_{10})$	0.065
$T(C_{29}-O)$	0.19				

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES FOR THE INFRARED ACTIVE VIBRATIONS OF THE PALLADIUM(II) CHELATE

Obsd cm <sup>-1</sup>	Calcd cm <sup>-1</sup>	Description	Obsd cm <sup>-1</sup>	Calcd cm <sup>-1</sup>	Description
3294	3294	NH <sub>2</sub> asym. str.	976		
3239	3247	NH <sub>2</sub> sym. str.		941	C=C def. + C <sub>10</sub> -C str.
3159	3159	OH str.	932		CH <sup>a)</sup> out of plane bending of benzene ring
3125					
3029		CH <sup>a)</sup> str. of benzene ring	860	901	CH <sub>2</sub> rocking + CH <sub>2</sub> -C str.
2976			837	837	CH <sub>2</sub> -C str. + CH <sub>2</sub> rocking
2951	2950	CH str.	805		
2919	2905	CH <sub>2</sub> asym. str.	782	797	CH <sub>2</sub> rocking + CCC def.
2849	2860	CH <sub>2</sub> sym. str.		740	C-O str. + C=C str.
2784			724		
2694			707		
1636	1630	CO <sub>2</sub> asym. str.	668	663	C-O torsion
	1620	C=C str.	660		
1584	1583	NH <sub>2</sub> scissors	641		
	1581	C=C str.	622		
1503	1523	C=C str.	613	647	NH <sub>2</sub> rocking
1433	1440	CH <sub>2</sub> scissors		627	C-CO <sub>2</sub> str. + CCC def.
1357	1369	CO <sub>2</sub> sym. str. + CH bending	583	586	CO <sub>2</sub> wagging
1321	1339	CH <sub>2</sub> wagging + CH bending		559	C=C torsion
	1315	CH bending + CH <sub>2</sub> wagging	542	541	CO <sub>2</sub> rocking + C <sub>10</sub> -C str.
1306	1301	CH bending + C=C str.	524		
1290		CH <sup>a)</sup> in plane bending of benzene ring	486	519	CO <sub>2</sub> rocking + C=C def.
1261	1277	C=C str.	432	517	C=C def.
	1231	CH bending + CH <sub>2</sub> wagging	429	412	C=C torsion
1205	1204	CH <sub>2</sub> twisting + COH def.	407	410	M-N str. + CCCN asym. def.
	1174	COH def. + C=C str.	392	397	CCO def. + C-C in plane def.
1171		CH <sup>a)</sup> in plane bending of benzene ring	377	367	C=C def. + C-O in plane def.
1151			342	351	CO out of plane def. + CCCN sym. def.
1137					
1097	1085	NH <sub>2</sub> wagging	317	311	CCCN asym. def. + CCO def.
1084				257	C <sub>10</sub> -C torsion + C <sub>5</sub> -C torsion
	1085	C=C str.		248	CCCN asym. def. + M-N str.
1062	1054	C-N str. + NH <sub>2</sub> twisting		228	C <sub>10</sub> -C <sub>13</sub> out of plane def. + C=C torsion
	1048	NH <sub>2</sub> twisting			
1021		CH <sup>a)</sup> in plane bending of benzene ring		216	O-M str. + CCCN asym. def.
	999	CO <sub>2</sub> scissors + C-CO <sub>2</sub> str.			

a) As the CH groups on the phenolic groups are considered as a single unit, the frequencies corresponding to the stretching and deformation vibrations of those groups will not appear in the calculations.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES RELATED TO THE METAL-LIGAND BOND (cm<sup>-1</sup>)

	Pd(II)		Cu(II)		Zn(II)		Cd(II)		Ni(II)		Co(II)	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
NH <sub>2</sub> asym. str.	3294	3294		3355	3348	3363	3345	3363	3359	3358	3277	3285
NH <sub>2</sub> sym. str.	3239	3247	3307	3306	3328	3314	3331	3314	3302	3308	3244	3238
OH str.	3159	3159	3255	3256	3267	3267	3283	3283		3209	3159	3159
COO <sup>-</sup> asym. str.	1636	1630	1630	1622	1597	1588	1608	1602	1625	1623	1629	1623
NH <sub>2</sub> scissors	1584	1583	1591	1587	1570	1575	1584	1584	1592	1598	1610	1616
COO <sup>-</sup> sym. str.	1357	1369	1373	1388	1357	1368	1357	1371	1391	1387	1378	1388
OH in plane def.	1205	1204	1235	1234	1242		1231	1230	1247	1240	1237	1233
NH <sub>2</sub> wagging	1097											
	1084	1085	1085	1088	1081	1074	1077	1078		1033		1047
OH out of plane def.	668	663	650	647	665	664	672	664	650	647	658	664
NH <sub>2</sub> rocking	613	647		642	603	587	599	601	587	582	582	584
COO <sup>-</sup> wagging	583	586		574	590	591	572	574	577	574		574
COO <sup>-</sup> rocking	486	519	486	522	498	503	496	503	494	521	487	519
MN str.	407	410	393	385	359	357	316	330	317	327	315	325

TABLE 6. VALUES OF FORCE CONSTANTS AND  $F_{\text{dia}}$  RELATED TO THE METAL-LIGAND BONDS

Force constant (mdyn/Å)	Pd(II)	Cu(II)	Zn(II)	Cd(II)	Ni(II)	Co(II)
$K(\text{MN})$	0.75	0.52	0.33	0.20	0.14	0.12
$K(\text{NH})$	5.68	5.90	5.93	5.93	5.91	5.65
$K(\text{C}_7\text{-O}_8)$	8.30	8.00	7.90	8.10	8.00	8.00
$K(\text{C}_7\text{-O}_9)$	5.60	6.10	5.80	5.80	6.00	6.10
$K(\text{C}_{29}\text{-O}_{32})$	2.50	2.50	2.50	2.50	2.50	2.50
$K(\text{OH})$	5.27	5.62	5.66	5.72	5.45	5.27
$H(\text{MNH})$	0.15	0.14	0.10	0.11	0.10	0.10
$H(\text{HNH})$	0.57	0.57	0.55	0.56	0.59	0.60
$H(\text{CCO})$	0.40	0.45	0.35	0.35	0.50	0.45
$H(\text{CCO}_R)$	0.50	0.50	0.35	0.35	0.50	0.50
$H(\text{OCO})$	0.35	0.35	0.35	0.35	0.35	0.35
$H(\text{C}_{13}\text{OH})$	0.30	0.40	0.40	0.40	0.43	0.40
$T(\text{COH})$ mdyn·Å	0.19	0.18	0.19	0.19	0.18	0.19
$P(\text{OCO})$ mdyn·Å	0.50	0.48	0.51	0.48	0.48	0.48
$F_{\text{dia}}(\text{NH}_2 \text{ asym. str.})$ mdyn/Å	5.90	6.12	6.15	6.15	6.13	5.87
$F_{\text{dia}}(\text{COO}^- \text{ asym. str.})$ mdyn/Å	7.27	7.37	7.17	7.27	7.32	7.37
$F_{\text{dia}}(\text{MN str.})$ mdyn/Å	0.98	0.75	0.56	0.43	0.37	0.35
$F_{\text{dia}}(\text{NH}_2 \text{ rocking})$ mdyn·Å	0.41	0.41	0.41	0.41	0.36	0.38
$F_{\text{dia}}(\text{CO torsion})$ mdyn·Å	0.19	0.18	0.19	0.19	0.18	0.19

strengths of the forces opposing the corresponding vibrational modes.

The values for the M-N bond-stretching force constants and the values of  $F_{\text{dia}}$  (M-N str.) vary in the order Pd(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II) > Co(II), which demonstrates a corresponding order in the strengths of the metal-nitrogen bonds.

Similar trends are found for the M-N stretching, the  $\text{NH}_2$  wagging, and the  $\text{NH}_2$  rocking frequencies.

The frequencies of  $\text{NH}_2$  scissors vibrations show a different trend. This may be due to an overlap with the  $\text{COO}^-$  stretching and C=C stretching vibrations to some extent.

These facts show that the phenolic group in the  $\beta$ -position of DL-tyrosine has no influence on the order of metal ligand bond strengths which has already been found in aliphatic  $\alpha$ -amino acid chelates.

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