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The metal complexes of amino acids and their *N*-substituted derivatives—VII. The i.r. spectra and normal coordinate analyses of bivalent metal complexes with *N*-methylglycine and *N*-phenylglycine

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Abstract—Twelve complexes of bivalent metals with *N*-methylglycine (sarcosine) and *N*-phenylglycine have been prepared over wide pH ranges and characterized by means of i.r., powder diffuse reflection, electronic spectra and magnetic susceptibility. These complexes are classified into two types, either with or without chloride ions, from elemental analyses: the former type (A) consists of $ML_2 \cdot nH_2O$ (M = Co, Ni, Cu, Zn for L = sarcosinate anion; M = Co, Ni, Cu, Zn, Cd for L = *N*-phenylglycinate anion), which appear to be octahedral complexes. The metal is coordinated through a nitrogen atom, a carboxyl oxygen atom and water molecules or the carboxyl oxygen atoms of neighboring molecules. The latter type (B) consists of $CoCl_2\,(HL)_2 \cdot 2H_2O$, $ZnCl_2\,(HL)_2$ and $CdCl_2\,(HL)$ (HL = sarcosine), in which the ligand has a zwitterion structure and has metal ions coordinated through only a carboxyl oxygen atom, but does not chelate through a nitrogen atom. In the cadmium (II) complex, a chloride ion seems to bridge to two cadmium (II) ions. In order to assign the observed frequencies of i.r. spectra in detail, normal coordinate analyses have been carried out for the complexes of the A type. The frequency separation of COO^- antisymmetric and symmetric vibrations of A type complexes with sarcosine increases in the order: Co (II) < Ni (II) < Zn (II) < Cu (II). These separations of A type complexes with sarcosine and *N*-phenylglycine are larger than those of the corresponding complexes with glycine, alanine and other α-amino acids. The frequencies of metal–nitrogen and metal–oxygen stretching vibrations increase in the order: Co (II) < Zn (II) < Ni (II) < Cu (II) for sarcosine A type complexes.

INTRODUCTION

Our laboratory investigates the spectral properties [1, 2] and crystal structures [3, 4] of the metal complexes of various amino acids and their derivatives. The present study is part of that program.

Many studies have been reported about the i.r. spectra of *N*-methylglycine (sarcosine) [5–9]. However there are few systematic studies about the metal complexes of sarcosine in the solid state. SVATOS *et al.* [10] discussed the NH stretching vibrations of the copper(II) and zinc(II) complexes of this ligand. The Raman and i.r. spectroscopy of tris(*N*-methylglycine) calcium(II) chloride has been reported by CHEN *et al.* [11].

Very little work on *N*-phenylglycine has been reported. NAKAMOTO *et al.* [12] reported the relation between the carboxyl stretching frequencies and the strength of the metal–oxygen interaction about some metal complexes of both ligands.

In this work, we discuss how the *N*-substituted methyl and phenyl groups influence the frequencies of i.r. spectra, in comparison with other α-amino acids complexes. For this purpose, we have prepared twelve bivalent metal complexes of sarcosine and *N*-phenylglycine over wide pH ranges. We then systematically investigated their i.r. and electronic spectra and magnetic susceptibility. In addition, normal coordinate analyses have been accomplished for A types of both ligands, for the detailed assignments of i.r. spectra.

EXPERIMENTAL

Preparation of compounds

Sarcosine: nickel(II)–A complex was prepared from 10 mmol of basic nickel(II) carbonate and 20 mmol of sarcosine by almost the same procedure as the threonine nickel(II) complex [13].

Copper(II)–A complex was prepared by the same procedure as the nickel(II)–A complex.

Zinc(II)–A and cobalt(II)–A complexes were prepared by adding 5 mmol of metal chloride to a hot solution containing 20 mmol of sarcosine and 10 mmol of sodium hydroxide.

Zinc(II)–B complex was prepared by adding 20 mmol zinc(II) chloride to a hot solution containing 20 mmol of sarcosine. The solution was condensed in a water bath. The colorless precipitate which formed was filtered, washed with ethanol several times, and left in a silica-gel desiccator.

Cobalt(II)–B and cadmium(II)–B complexes were prepared by means of almost the same procedure as that for the zinc(II)–B complex, except that the precipitate was washed with methanol for cobalt(II)–B.

N-Phenylglycine: all complexes were prepared from 5 mmol of metal chloride, 10 mmol of *N*-phenylglycine and 10 mmol of sodium hydroxide.

Deuterated compounds: for sarcosine and its metal complexes these were prepared by the procedure used for DL-serine and its complexes [1], and for *N*-phenylglycine complexes these were prepared by the procedure mentioned above in deuterium oxide.

Magnetic susceptibility and optical measurements

Magnetic susceptibility, powder diffuse reflection spectra, electronic spectra, and i.r. spectra were obtained by the methods used for the complexes with 4-hydroxy-L-proline [2] and DL-threonine [13].

RESULTS AND DISCUSSION

From the results of elemental analyses sarcosine complexes are classified into two distinct types which either do or do not have chloride ions: the first type includes $ML_2 \cdot 2H_2O$ (M = Co(II), Ni(II), Cu(II), Zn(II) for $L = CH_3NHCH_2COO^-$). $CoCl_2(HL)_2 \cdot 2H_2O$, $ZnCl_2(HL)_2$ and $CdCl_2(HL)$ are the second type. We call the first type A, and the second one B for convenience. All *N*-phenylglycine complexes are A type.

Electronic spectra and magnetic moments

The results of elemental analyses and other physical properties are listed in Table 1.

Sarcosine: the electronic and reflection spectra of the nickel(II)–A complex are similar to those of diaquabis(glycinato)nickel(II) [14, 15]. It was reported by an X-ray analysis that diaquabis(sarcosinato)nickel(II) has a *trans* octahedral configuration [16]. Therefore the bands at about 610 and 370 nm are assigned as shown in Table 1. Copper(II)–A probably has a *trans* configuration, because for bis(glycinato)copper(II) monohydrate, the *trans* complex has the reflection band at 619 nm and the *cis* one has it at 648 nm [17], and the i.r. spectra of copper(II)–A, are similar to those of nickel(II)–A which has a *trans* configuration. The band at 495 nm for cobalt(II)–A is assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ in an O_h approximation as the high spin octahedral cobalt(II) complex has the absorption bands in this visible region. However cobalt(II)–B complex has two reflection peaks at 530 and 480 nm. This split seems to be due to the decrease of the symmetry by coordination of chloride ions. For both cobalt(II) complexes, the magnetic moments are within the ranges expected for high spin octahedral complexes (4.7–5.2 B.M. for cobalt(II)) [18].

N-phenylglycine: the reflection spectra and magnetic moments of *N*-phenylglycine complexes are similar to those of sarcosine A type complexes.

Infrared absorption spectra

Assignment of observed frequencies. The assignments of observed frequencies for metal complexes with sarcosine and *N*-phenylglycine have been made by comparison with those of sarcosine [5–12], glycine [19–22], DL-α-serine [1], *N*-tris(hydroxymethyl)methylglycine [23], phenylalanine [24], and these metal complexes. The spectra of these metal complexes are shown in Figs 1, 2, 3 and 4. The spectra of *N*-phenylglycine complexes are similar to each other except copper(II) complex which is anhydrous, and more complicated than those of sarcosine ones, owing to the benzene ring. The observed bands of benzene ring were assigned by referring to the assignment of phenylalanine [24] and toluene [25]. The observed frequencies and assignments for sarcosine and the metal complexes are listed in Table 2(a), and

Table 1. Analytical data and physical properties of sarcosine and *N*-phenylglycine complexes

	Found (calcd.)					Magnetic moment	Reflection spectra	Electronic spectra
Complexes	H (%)	C (%)	N (%)	M (%)	Cl (%)	μ_{eff}/μ_B	λ (nm)	λ (nm)
$Co(sar)_2 \cdot 2H_2O$	5.95 (5.95)	26.50 (26.58)	10.31 (10.33)	20.7 (21.74)	0 (0)	4.87* (3.87)	495	insoluble†
$Ni(sar)_2 \cdot 2H_2O$	5.96 (5.95)	26.54 (26.60)	10.34 (10.34)	22.8 (21.67)	0 (0)	3.19 (2.83)	603, 385	610, 370
$Cu(sar)_2 \cdot 2H_2O$	5.79 (5.85)	26.16 (26.13)	10.36 (10.16)	23.6 (23.04)	0 (0)	1.92 (1.73)	603	618
$Zn(sar)_2 \cdot 2H_2O$	5.76 (5.81)	25.90 (25.96)	10.15 (10.09)	23.7 (23.55)	0 (0)	dia	—	—
$CoCl_2(Hsar)_2 \cdot 2H_2O$	5.27 (5.27)	20.97 (20.95)	8.28 (8.14)	16.8 (17.13)	20.52 (20.61)	5.07 (3.87)	530, 480	510, 482
$ZnCl_2(Hsar)_2$	4.44 (4.49)	22.70 (22.92)	8.69 (8.91)	20.9 (20.79)	22.55 (22.55)	dia	—	—
$CdCl_2(Hsar)$	2.53 (2.59)	13.18 (13.23)	5.06 (5.14)	40.8 (41.27)	25.90 (26.03)	dia	—	—
$Co(npg)_2 \cdot 2H_2O$	5.05 (5.10)	48.52 (48.62)	7.06 (7.09)	14.6 (14.91)	0 (0)	4.72 (3.87)	530, 498	insoluble
$Ni(npg)_2 \cdot 2H_2O$	5.13 (5.10)	48.77 (48.65)	7.12 (7.09)	13.3 (14.86)	0 (0)	3.17 (2.83)	665, 395	insoluble
$Cu(npg)_2$	4.37 (4.43)	52.07 (52.82)	7.56 (7.70)	17.7 (17.46)	0 (0)	1.82 (1.73)	575, 395	insoluble
$Zn(npg)_2 \cdot 2H_2O$	4.95 (5.02)	47.38 (47.84)	6.86 (6.97)	16.4 (16.27)	0 (0)	dia	—	—
$Cd(npg)_2 \cdot 2H_2O$	4.47 (4.49)	42.94 (42.82)	6.21 (6.24)	24.8 (25.05)	0 (0)	dia	—	—

*( ): Spin only value.

†Electronic spectra were obtained in 1 mol dm^{-3} $NaClO_4$. Hsar = sarcosine, Hnpg = *N*-phenylglycine.

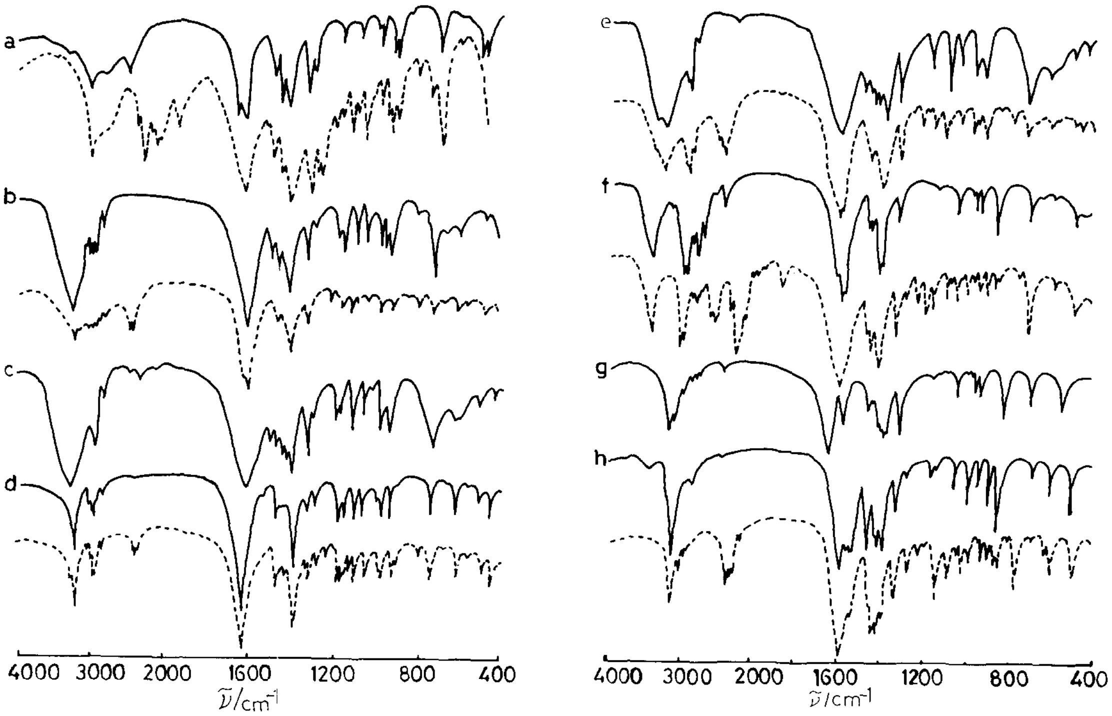

Fig. 1. Infrared absorption spectra of sarcosine, its complexes (——) and these deuterated compounds (----) in KBr disks. (a) = Sarcosine, (b) = Co(II)-A, (c) = Ni(II)-A, (d) = Cu(II)-A, (e) = Zn(II)-A, (f) = Co(II)-B, (g) = Zn(II)-B, (h) = Cd(II)-B.

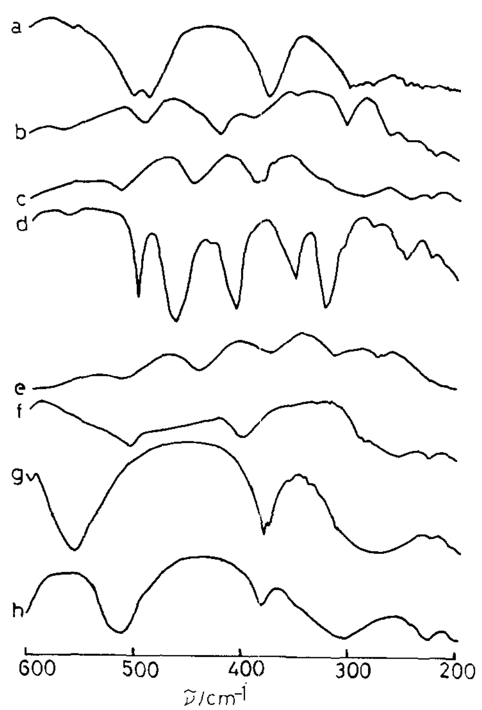

Fig. 2. Far i.r. absorption spectra of sarcosine and its metal complexes in Nujol. (a) = sarcosine, (b) = Co(II)-A, (c) = Ni(II)-A, (d) = Cu(II)-A, (e) = Zn(II)-A, (f) = Co(II)-B, (g) = Zn(II)-B, (h) = Cd(II)-B.

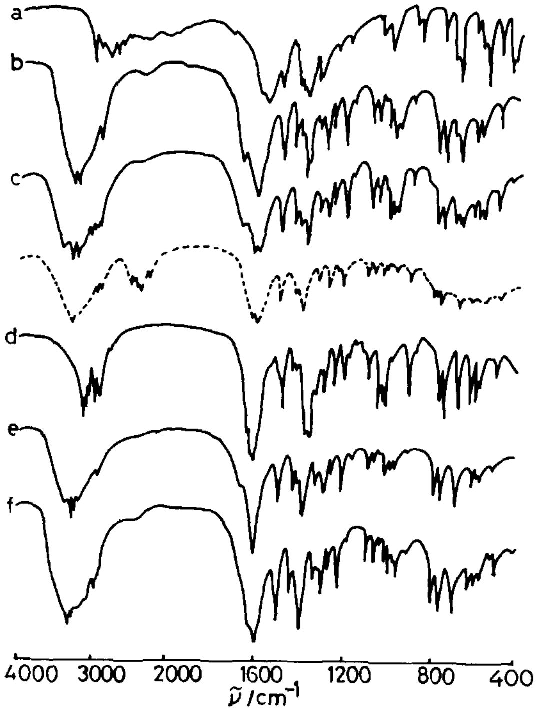

Fig. 3. Infrared absorption spectra of *N*-phenylglycine, its complexes (——) and these deuterated compounds (----) in KBr disks. (a) = *N*-Phenylglycine, (b) = Co(II), (c) = Ni(II), (d) = Cu(II), (e) = Zn(II), (f) = Cd(II).

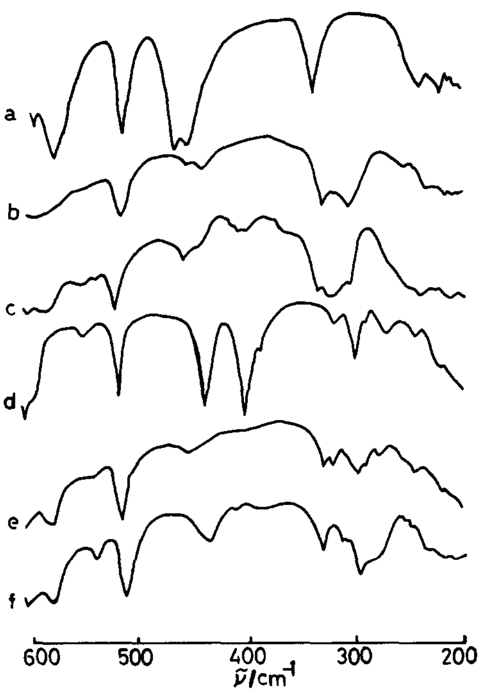

Fig. 4. Far i.r. absorption spectra of *N*-phenylglycine and its metal complexes in Nujol. (a) = *N*-phenylglycine, (b) = Co(II), (c) = Ni(II), (d) = Cu(II), (e) = Zn(II), (f) = Cd(II).

those of *N*-phenylglycine and the metal complexes are listed in Table 2(b).

A type complexes containing no chloride ions. The spectra of the A type complexes with sarcosine are similar. For sarcosine complexes, the sharp band at about 3240 cm^{-1} and the broad bands above 3200 cm^{-1} which are not observed for the free ligand, shift to lower frequency regions on deuteration. So, these bands are assigned to NH and OH stretching vibrations of the water molecule, respectively. For same reason, the bands above 3200 cm^{-1} of *N*-phenylglycine complexes are assigned as shown in Table 2(b).

From 1800 to 600 cm^{-1}, for A type complexes with both ligands, only one peak shifts to lower frequency regions on deuteration: this one is assigned to NH bending vibration because it cannot be observed for the free ligand.

All complexes have broad strong bands at about 1600 and 1400 cm^{-1}, which are assigned to COO$^-$ antisymmetric and symmetric stretching vibrations [26].

From 600 to 200 cm^{-1}, A type complexes with both ligands have very similar spectra in this region, respectively. As diaquabis(sarcosinato)nickel(II) is centrosymmetric and has a *trans* octahedral configuration from X-ray analysis [16], only the antisymmetric metal–ligand stretching vibrations are i.r.-active. In this region, absorption bands which cannot be observed in the free ligand appear in A type complexes. These are assigned to the M–N and M–O stretching vibrations by comparing these spectra with those of the metal complex with glycine [20–22] as shown in Tables 2(a) and 2(b).

B Type complexes containing chloride ions. For the cobalt(II)–B complex, the broad band at 3405 cm^{-1} can be assigned to the OH stretching vibration of the water molecule, because it shifts to about 2600 cm^{-1} on deuteration, and is not observed for zinc(II)–B and cadmium(II)–B complexes which have no water molecules. The bands from 2967 to 2411 cm^{-1} disappear on deuteration, too. Therefore these bands are assigned to the NH_2^+ stretching vibrations by considering the bands at about 1600 cm^{-1} and the results of the elemental analysis.

The bands at 3165, 3080 and from about 2850 to 2750 cm^{-1} for zinc(II)–B complex, and the band at 3130 cm^{-1} for cadmium(II)–B complex disappear on deuteration. So these are due to the NH_2^+ stretching vibrations, as in the cobalt(II)–B complex.

As shown in Table 2(a), cobalt(II)–B complex shows the NH_2^+ stretching vibrations at a lower frequency region than that for zinc(II)–B and cadmium(II)–B. This result seems to be due to a weakening of the NH bond strength by the hydrogen bond with the water molecule.

From 1800 to 600 cm^{-1}, for B type complexes, several peaks disappear on deuteration. By considering the bands above 2500 cm^{-1}, we think that the NH_2^+ group may be retained in B type complexes and these bands are assigned to NH_2^+ scissors, wagging and rocking vibrations.

For zinc(II)–B, cobalt(II)–B and cadmium(II)–B complexes the frequency separation of COO$^-$ antisymmetric and symmetric stretching vibrations are *ca* 250, 175 and 168 cm^{-1}, respectively. It is well known that for the metal complexes of carboxylic acids the carboxylate ion may coordinate to a metal in three ways: unidentate, bidentate (chelate) and bridging complexes. The separation of both vibrations is much larger in unidentate complexes than in the free ion, while it is smaller in bidentate(chelate) complexes than in the free ion. In the bridging complex, the frequencies of two COO$^-$ stretching vibrations are close to the free ion values [26]. Therefore, in zinc(II)–B complex, the carboxylate ion seems to coordinate to a metal ion as a unidentate ligand, but in cobalt(II)–B and cadmium(II)–B complexes this ion seems to coordinate as a bidentate or a bridging ligand. Identical results were observed for dichloro(L-proline)cadmium(II) hydrate [4] and dichloro–bis(L-proline)zinc(II) [27], whose structures have been determined by X-ray analyses.

In the far i.r. region, the spectra of B type complexes are simpler than those of A type complexes and are similar to that of the free ligand. There are no bands at about 420 cm^{-1}, where A type complexes have bands due to the M–N antisymmetric stretching vibration. The M–N bond seems to be absent in B type and cadmium(II)–B complexes. Therefore, in these three

Table 2(a). Assignments of i.r. absorption spectra of sarcosine and its metal complexes (cm^{-1})*

Ligand	Co(II)–A	Ni(II)–A	Cu(II)–A	Zn(II)–A	Co(II)–B	Zn(II)–B	Cd(II)–B	Assignments
					3405 s			H_2O
	3243 sb	3247 sb	3190 s	3235 vsb				NH str.
						3165 s	3130 s	NH_2^+ str. (ligand
						3080 s		and B complexes)
3026 s						3028 sh		
3006 s	2998 w	3002 w	3009 vw	3002 vw	3002 s	2991 vw	3008 sh	CH_3 deg. str.
	2970 w	2977 w	2975 sh	2978 sh	2967 s			
	2956 w	2956 w	2958 m	2958 sh		2957 w	2950 vw	CH_2 asym. str.
	2923 w	2930 m	2932 m	2929 m		2932 sh	2923 vw	CH_2 sym. str.
	2887 w	2897 sh	2898 sh	2902 sh				CH_3 sym. str.
	2866 w		2854 w	2856 sh	2851 w	2851 vw	2841 w	+
2820 sh	2805 w	2816 w	2805 w	2817 sh	2789 m	2801 vw	2770 vw	
2750 s						2751 vw		NH_2^+ str. (ligand and B
					2707 m			complexes)
2649 sh								
2454 m					2411 m			
1643 s					1622 sh	1654 sh	1601 sh	NH_2^+ scissors (ligand)
1604 s	1602 sb	1599 sb	1624 s	1604 sb	1591 s	1643 s	1584 m	COO^- asym. str.
					1574 sh	1573 sh	1560 sh	NH_2^+ scissors
						1560 sh	1554 sh	(B complexes)
1490 sh	1486 m	1489 m	1469 m	1489 m			1534 s	NH bending
1471 m	1462 m	1459 m	1457 w	1459 m	1476 m	1460 m	1460 s	CH_3 deg. def.
1440 m	1445 sh	1437 m	1448 w	1440 m	1456 m	1441 w	1430 sh	CH_2 wagging
1408 s	1425 sh	1420 m	1417 w	1422 m		1422 sh		CH_2 scissors
	1410 s	1397 s	1384 s	1395 s	1416 s	1405 sh	1416 s	COO^- sym. str.
1384 sh					1400 s	1389 m	1393 s	NH_2^+ wagging (ligand
						1378 sh		and B complexes)
1304 m	1319 m	1318 m	1316 m	1318 s	1325 m	1311 m	1319 m	CH_2 wagging
1288 m	1289 w	1288 w	1272 m	1294 sh			1275 w	C–N str.
	1179 w	1175 w	1179 m	1173 m				
1165 vw	1158 m	1163 m	1165 m	1165 m	1163 vw	1153 w	1156 w	CH_2–C str.
1146 w		1143 sh	1154 m		1143 vw	1130 vw	1139 w	CH_3 rocking
			1112 m					
	1099 m	1099 m	1105 m	1098 m				
1065 w								
	1041 m	1039 m	1060 m	1037 m	1050 m	1041 w	1049 m	N–C str.
995 w		1017 w						
974 m	980 m	974 m	987 sh	970 m	980 w	976 vw	984 m	
	953 m	958 sh	972 m	962 sh	964 m	956 m		N–C str.
932 w	932 m	928 m	931 m	921 m	938 m	929 m	939 m	CH_2 rocking + N–C
924 m						921 m		str.
905 m			909 w					
896 m					862 m		887 m	NH_2^+ rocking (ligand
							854 sh	and B complexes)
							848 m	
	808 w					821 m		C–C str.
700 m	738 m	731 m	743 m	726 m	711 m	699 m	686 w	COO^- scissors
					667 w			
594 sh	617 w	620 mb	626 m	625 m	601 w	595 w	607 m	COO^- wagging
501 m	572 sh	595 m		588 sh				
484 m	491 w	512 m	496 m	512 w	502 m	552 m	511 m	COO^- rocking
	420 m	444 m	461 m	422 w				M–N str.
376 m	386 w	387 m	407 m	373 w	397 w	377 w	378 w	skeletal def.
	342 vw		348 w					
	304 m	314 m	322 m	313 w			304 m	M–O str.
293 w		292 m			291 sh	292 m	292 sh	skeletal def.
		283 sh			283 sh	282 m	283 w	
					269 m	269 m		M–O str.
	266 m	254 m	275 vw	275 w				skeletal def.
		249 m	247 w					
234 w	225 wb	223 w	221 vw		235 vw		235 m	N–C torsion
218 w								

*Abbreviations: s = strong; m = medium; w = weak, v = very; sh = shoulder; b = broad.

Table 2(b). Assignments of i.r. absorption spectra of *N*-phenylglycine and its metal complexes (cm^{-1})*

Ligand	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Assignments
		3382 m				
	3288 s	3278 s		3286 m	3289 s	NH str. + H_2O
	3234 s	3220 s		3227 m	3243 s	
3104 sh		3170 sh	3142 m		3104 sb	
3053 sh			3090 m			NH_2^+ str. (ligand)
3020 m	3059 wsh	3058 w	3057 m	3060 wsh	3065 wsh	CH str. of benzene ring
	2992 w	2985 w		2989 w	2997 wsh	
2947 m	2955 wsh	2965 w	2964 m			NH_2^+ str. (ligand)
	2916 m	2927 w				CH_2, CH str.
			2913 m	2915 w	2915 w	
2847 sh			2825 vw			
2794 mb			2787 vw			
2713 m						
2631 sh						
1562 vsb	1601 s	1595 sb	1616 s	1594 vs	1594 vs	COO$^-$ asym. str. + ν16†, ν 16′ + NH_2^+ scissors
1485 m	1490 m	1487 s	1491 s	1490 m	1492 m	NH bending (complexes) + ν13
1416 m	1439 m	1437 m	1444 vw	1437 m	1439 m	CH_2 scissors
1401 sh	1416 sh	1413 w	1422 vw	1413 w		
1382 s	1392 s	1389 s	1385 s	1390 s	1389 s	COO$^-$ sym. str.
1322 m	1323 w	1322 m	1329 vw	1321 m	1323 w	CH_2 wagging
1310 m						
1299 sh	1300 vw	1300 vw		1301 vw		
1282 sh	1286 m	1283 m	1291 m	1282 m	1285 m	CH_2 twisting
	1258 w	1254 m	1245 m	1252 w	1256 m	CH_2 wagging
1229 w	1210 m	1201 m	1200 m	1205 m	1211 m	C–C str.
1185 w	1181 vw	1184 vw			1188 vw	CH_2 rocking
1160 vw	1156 vw	1168 vw	1155 vw	1153 w	1174 vw	
	1148 vw	1150 vw	1115 vw			
1128 sh						
1108 sh						
1073 vw	1087 w	1086 m	1094 m	1084 w	1085 w	ν 14′
		1065 sh				
1037 w	1058 w	1054 m	1058 w	1058 w	1059 w	ν 14
			1044 m			
1027 sh		1027 w	1028 m	1028 w	1031 vw	N–C str.
1000 sh	1014 m	1011 m		1009 w	1007 w	ν 6
996 m	996 m	990 m	997 w	991 w	992 w	ν 19′ + NH_2^+ twisting (ligand)
982 vw		980 m				ν 7′
	966 m	973 m		965 w	953 m	N–C str.
913 vw	912 w	911 w	919 m	909 w	906 vw	CH_2 rocking + C–C str.
879 w						NH_2^+ rocking
862 m						
780 vw	791 m	789 m	780 m	789 m	786 m	COO$^-$ scissors
763 m	768 m	764 m	756 s	765 m	767 m	C–C str. + ν 4
707 sh	713 sh	713 w				
691 s	683 m	692 m	693 m	682 m	682 m	ν 8
665 sh						
620 w	628 m	630 m	637 m	628 m	626 w	COO$^-$ wagging
595 m	592 m	604 w	606 m	604 m	602 w	
578 s	587 m	587 w	598 sh	582 m	579 w	ν 18′
			552 w		538 vw	
515 m	515 m	520 w	518 m	516 m	511 w	COO$^-$ rocking
465 m	455 vw					
454 m	437 vw	458 w	437 m	453 w	433 w	ν 20
	410 vw	408 m	402 m	405 vw	409 vw	M–N str.
					385 vw	
338 m	331 m	336 m	317 w	329 w	328 w	skeletal def.
				319 w	312 vw	
	308 m	324 m	300 m	300 mb	296 w	M–O str.
302 vw	301 m	303 vw				
289 vw	288 vw	290 vw	269 w	277 w	278 vw	skeletal def.
241 m	240 sh	238 sh	245 w	244 w	237 sh	
221 m		219 sh	222 w	221 w	221 vw	N–C torsion

*Abbreviations: s = strong; m = medium; w = weak, v = very; sh = shoulder; b = broad.

†The numbering system used for the benzene ring vibrations is that of HERZBERG [28], as recommended by the Joint Commission for Spectroscopy [29].

complexes, the NH_2^+ group may be retained and the nitrogen atom may not coordinate to the metal ion.

B type complexes have broader bands from 300 to 250 cm^{-1} than the free ligand has. These bands seem to be partially associated with the M–O antisymmetric stretching vibration.

Normal coordinate analyses

The normal coordinate analyses were performed as a 25 body problem for the A type complexes with sarcosine, and a 19 body problem for *N*-phenylglycine complexes, in which a phenyl group is considered as one unit. The calculations were carried out on the HITAC M-200H computer at the Computer Center of the University of Tokyo. GUHA [16] carried out a crystallographic investigation of diaquabis(sarcosinato)nickel(II). He reported that the molecule was centrosymmetric and that nickel(II) was coordinated through a nitrogen atom, a carboxyl oxygen atom and two water molecules. Therefore, the model adopted for the calculations is such that the five-membered chelate ring is planar and the molecule has *Ci* symmetry, as shown in Fig. 5.

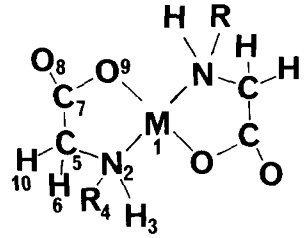

Fig. 5. Structure of *N*-substituted glycine A type complexes. R = CH_3 for sarcosine, R = P for *N*-phenylglycine.

The same bond lengths and bond angles were used in calculation for both sarcosine and *N*-phenylglycine complexes; they are listed in Table 3. The frequencies for the i.r. active species were calculated using the symmetry coordinates listed in Table 4. WILSON'S *GF* matrix method [30] was used, and all results were obtained using a FORTRAN program designed by SHIMANOUCHI [31]. The force field employed was the Urey–Bradley type; and the force constants reported for DL-threonine complexes [13] were used as the initial values. The remaining force constants were evaluated so as to obtain the best fit between the calculated and observed frequencies by a trial and error method, guided by the values of the Jacobian matrix. The force constants used in this calculation are listed in Table 5. Tables 6(a) and 6(b) show the observed and calculated frequencies, potential energy distributions to symmetry coordinates and force con-

Table 3. Bond lengths and bond angles used in the calculation for sarcosine and *N*-phenylglycine complexes

Bond angles (°)			
O–M–N	85.219065*	C–C–O_9	119.88904*
M–N–C	$\theta^{\dagger}$	C–C–O_8	115.2
N–C–C	θ	C–O–M	115.95857*
Bond lengths (Å)			
M–N	2.046	N_2–R_4	1.474
N_2–C_5	1.465	C_5–C_7	1.520
C–H	1.09	N–H	1.01
C–O_9	1.282	C–O_8	1.207
O–M	1.880		

*Calculated value. All other angles are assumed to be tetrahedral angles. The same bond lengths and bond angles are used for second chelate ring.

$^{\dagger}\theta$: tetrahedral angle.

Table 4. Symmetry coordinates of i.r. active species for sarcosine and *N*-phenylglycine complexes

Description of coordinate		sarcosine	*N*-phenylglycine	Description of coordinate		sarcosine	*N*-phenylglycine
NH	str.	S_1	S_3	CH_3	deg. def. 2	S_{21}	
CH_2	asym. str.	S_2	S_5	CH_3	rocking 1	S_{22}	
CH_2	sym. str.	S_3	S_6	CH_3	rocking 2	S_{23}	
CH_3	deg. str. 1	S_4		NH	bending 1	S_{24}	S_{14}
CH_3	deg. str. 2	S_5		NH	bending 2	S_{25}	S_{15}
CH_3	sym. str.	S_6		CCNM	deg. def. 1	S_{26}	S_{12}
CO_2	asym. str.	S_7	S_8	CCNM	deg. def. 2	S_{27}	S_{13}
CO_2	sym. str.	S_8	S_9	CCNM	sym. def. 1	S_{28}	S_{11}
N_2–C_5	str.	S_9	S_4	CO_2	scissors	S_{29}	S_{21}
C_5–C_7	str.	S_{10}	S_7	CO_2	rocking	S_{30}	S_{22}
N–C_4	str.	S_{11}	S_{10}	COM	def.	S_{31}	S_{23}
M–N	str.	S_{12}	S_1	MO	bending	S_{32}	S_{24}
M–O	str.	S_{13}	S_2	MN	bending	S_{33}	S_{25}
CH_2	rocking	S_{14}	S_{17}	CO_2	wagging	S_{34}	S_{29}
CH_2	wagging	S_{15}	S_{16}	CO_2	twisting	S_{35}	S_{30}
CH_2	twisting	S_{16}	S_{18}	N_2–C_5	torsion	S_{36}	S_{31}
CH_2	scissors	S_{17}	S_{19}	N_2–C_4	torsion	S_{37}	
NCC	scissors	S_{18}	S_{20}	redundancy	N	S_{38}	S_{28}
CH_3	sym. def.	S_{19}		redundancy	C_4	S_{39}	
CH_3	deg. def. 1	S_{20}		redundancy	C_5	S_{40}	S_{27}
				redundancy	C_7	S_{41}	S_{26}

Table 5. Force constants used in the calculation for the nickel(II) complexes

Stretching (mdyn/Å)			Bending (mdyn/Å)			Repulsion (mdyn/Å)		
	Sarcosine	*N*-phenylglycine		Sarcosine	*N*-phenylglycine		Sarcosine	*N*-phenylglycine
K(NH)	5.36	5.28	H(HC5N)	0.32	0.32	F(HC5N)	0.54	0.54
K(CH)	4.27	4.30	H(HCC)	0.20	0.22	F(HCC)	0.36	0.35
K(CO8)	7.40	7.36	H(NC5C7)	0.20	0.20	F(NC5C7)	0.20	0.20
K(CO9)	6.30	6.26	H(HC4H)	0.417	—	F(HC4H)	0.04	—
K(N2C4)	2.12	—	H(NC4H)	0.35	—	F(NC4H)	0.54	—
K(N2C5)	2.12	2.12	H(HC5H)	0.372	0.37	F(HC5H)	0.06	0.06
K(C5C7)	1.50	1.50	H(HNM)	0.20	0.23	F(HNM)	0.08	0.05
K(MO)	0.69	0.79	H(HNC4)	0.35	—	F(HNC4)	0.50	—
K(MN)	0.85	0.56	H(HNP4)	—	0.35	F(HNP4)	—	0.50
K(CH_3)	4.46	—	H(HNC5)	0.35	0.35	F(HNC5)	0.50	0.50
K(N2P4)	—	1.98	H(C4NM)	0.05	—	F(C4NM)	0.10	—
Out-of-plane wagging (mdyn·Å)			H(P4NM)	—	0.05	F(P4NM)	—	0.10
P(COO^-)	0.55	0.57	H(C5NM)	0.05	0.05	F(C5NM)	0.10	0.10
			H(C4NC5)	0.20	—	F(C4NC5)	0.30	—
Torsion (mdyn·Å)			H(P4NC5)	—	0.20	F(P4NC5)	—	0.30
T(C5C7)	0.15	0.16	H(OCO)	0.92	0.92	F(OCO)	2.50	2.50
T(C5N2)	0.185	0.17	H(CCO8)	0.43	0.41	F(CCO8)	0.68	0.68
T(N2C4)	0.185	—	H(CCO9)	0.43	0.41	F(CCO9)	0.83	0.83
			H(COM)	0.05	0.05	F(COM)	0.10	0.10
			H(OMN_r)	0.05	0.05	F(OMN_r)	0.05	0.05
			H(OMN)	0.05	0.05	F(OMN)	0.05	0.05

Table 6(a). Observed and calculated frequencies and potential energy distributions among symmetry coordinates and force constants for the i.r. active vibrations of nickel(II) complex with sarcosine

Obsd. (cm^{-1})	Calcd. (cm^{-1})	PED in symmetry coordinate (%)	PED in force constants (%)	Description
3247	3246	S_1 (100)	K (NH) 91	NH str.
3002	2978	S_4 (81)	K (CH$_3$) 93	CH$_3$ deg. str.
2977	2977	S_5 (81)	K (CH$_3$) 93	CH$_3$ deg. str.
2956	2957	S_2 (101)	K (CH) 91	CH$_2$ asym. str.
2930	2916	S_3 (100)	K (CH) 88	CH$_2$ sym. str.
2897	2897	S_6 (99)	K (CH$_3$) 91	CH$_3$ sym. str.
2816				
1599	1599	S_7 (86)	K (CO8) 54, K (CO9) 29	CO$_2$ asym. str.
	1524	S_{19} (71), S_{25} (27)	H (NC4H) 29, H (HC4H) 25	CH$_3$ sym. def.
1489	1486	S_{25} (53), S_{19} (29)	H (HNC5) 20, H (HC4H) 18	NH bending + CH$_3$ sym. def.
1459	1460	S_{21} (78), S_{23} (20)	H (HC4H) 75, H (NC4H) 13	CH$_3$ deg. def.
	1457	S_{20} (64), S_{22} (19)	H (HC4H) 62, H (NC4H) 13	CH$_3$ deg. def.
1437	1434	S_{17} (58), S_{15} (25)	H (HC5H) 39, H (HC5N) 29	CH$_2$ scissors + CH$_2$ wagging
1420				
1397	1391	S_8 (77), S_{29} (37)	K (CO9) 32, K (CO8) 15	CO$_2$ sym. str.
1318	1314	S_{24} (37), S_{17} (25)	H (HC5H) 18, H (HNM) 15	NH bending + CH$_2$ scissors
1288	1286	S_{16} (69)	H (HC5N) 40, F (HC5N) 25	CH$_2$ twisting
	1249	S_{24} (39), S_{15} (37)	H (HNM) 18, H (HCC) 15	NH bending + CH$_2$ wagging
1175	1179	S_{23} (48), S_{22} (16)	H (NC4H) 40, F (NC4H) 23	CH$_3$ rocking
1163				
1143	1136	S_{22} (48), S_{23} (17)	H (NC4H) 41, F (NC4H) 23	CH$_3$ rocking
1099				
1039	1030	S_{29} (43), S_8 (22)	F (OCO) 40, H (OCO) 19	CO$_2$ scissors + CO$_2$ sym. str.
1017				
974	966	S_{11} (47), S_9 (41)	K (N2C4) 25, K (N2C5) 24	N$_2$–C$_4$ str. + N$_2$–N$_5$ str.
958				
928	924	S_9 (29), S_{11} (26)	K (N2C5) 17, K (N2C4) 14	N$_2$–C$_5$ str. + N$_2$–C$_4$ str.
	843	S_{14} (72), S_{11} (25)	H (HCC) 29, F (HCC) 18	CH$_2$ rocking + N$_2$–C$_4$ str.
731	730	S_{10} (48), S_{29} (14)	F (CCO9) 24, K (C5C7) 21	C$_5$–C$_7$ str.
620	618	S_{34} (99)	W (COO) 99	CO$_2$ wagging
595				
512	514	S_{30} (49), S_9 (12)	F (CCO8), 20, H (COO8) 18	CO$_2$ rocking + N$_2$–C$_5$ str.
444	442	S_{12} (64), S_{28} (22)	K (MN) 48	MN str.
387	387	S_{37} (73), S_{36} (24)	T (N2C4) 73, T (N2C5) 24	N$_2$–C$_4$ torsion
	333	S_{28} (41), S_{26} (13)	H (C4NC5) 24, F (C4NC5) 19	CCNM sym. def. + CCNM deg. def.
	331	S_{36} (54), S_{37} (25)	T (N2C5) 54, T (N2C4) 25	N$_2$–C$_5$ torsion + N$_2$–C$_4$ torsion
314	313	S_{13} (78), S_{18} (10)	K (MO) 66	MO str.
292				
283				
254	256	S_{26} (27), S_{32} (11)	H (C4NC5) 12, H 12	CCNM deg. def. + MO bending
249				
223	213	S_{35} (78), S_{36} (20)	T (C5C7) 78, T (N2C5) 20	CO$_2$ twisting

stants, with an approximate description of the vibration mode for the nickel(II)–A with sarcosine and *N*-phenylglycine. A similar calculation was accomplished for all A type complexes of sarcosine. Good agreement was obtained between the observed and calculated frequencies for these complexes. As shown in Tables 5 and 6(b), though the calculation was carried out considering a phenyl group as one unit for *N*-phenylglycine complexes, good agreement was obtained between the observed and calculated frequencies, except for one phenyl group. The values of force constants used in the calculation are approximately equal to those of sarcosine complexes. Therefore the skeletal vibrations of the chelate seem not to be influenced by the vibrations of a phenol group.

Metal–ligand bonds

Frequencies and force constants related to the metal–ligand bond are listed in Tables 7 and 8, respectively. In Table 8, the F_{dia} terms represent the diagonal elements of the symmetrized F matrix or the strength of the forces opposing the corresponding vibrational modes. As shown in Table 7, the frequency separation of COO$^-$ antisymmetric and symmetric vibrations of A type complexes with sarcosine increase in the order: cobalt(II) < nickel(II) < zinc(II) < copper(II). This trend has been observed for the corresponding series of complexes with various α-amino acids and these derivatives [21, 23, 32–34]. It suggests an increase in the degree of interaction of metal–oxygen bonds for the metal complexes given in the above order [26]. The frequencies of M–N and

Table 6(b). Observed and calculated frequencies and potential energy distributions among symmetry coordinates and force constants for the i.r. active vibrations of nickel(II) complex with *N*-phenylglycine

Obsd. (cm^{-1})	Calcd. (cm^{-1})	PED in symmetry coordinate (%)	PED in force constants (%)	Description
3220	3220	S_3 (100)	K (NH) 91	NH str.
2965	2965	S_5 (101)	K (CH) 91	CH_2 asym. str.
2927	2926	S_6 (100)	K (CH) 88	CH_2 sym. str.
1595	1595	S_8 (87)	K (CO8) 54, K (CO9) 29	CO_2 asym. str.
1487	1484	S_{15} (84)	H (HNC5) 32, H (HNP4) 23	NH bending
1437	1434	S_{19} (43), S_{16} (33)	H (HC5N) 36, H (HC5H) 23	CH_2 scissors + CH_2 wagging
1389	1389	S_9 (78), S_{21} (37)	K (CO9) 30, K (CO8) 17	CO_2 sym. str. + CO_2 scissors
1300	1297	S_{14} (60), S_{19} (28)	K (HNM) 29, H (HC5H) 16	NH bending 1 + CH_2 scissors
1283	1281	S_{18} (82)	H (HC5N) 41, F (HC5N) 26	CH_2 twisting
1254	1256	S_{16} (44), S_{14} (35)	H (HCC) 24, H (HNM) 18	CH_2 wagging + NH bending
1027	1032	S_{21} (43), S_9 (22)	F (OCO) 39, H (OCO) 19	CO_2 scissors + CO_2 sym. str.
973	969	S_4 (79), S_{22} (9)	K (N2C5) 46, F (HC5N) 16	N–C5 str.
911	893	S_{17} (91), S_{18} (13)	H (HCC) 44, F (HCC) 25	CH_2 rocking
764	739	S_7 (46), S_{21} (13)	F (CCO9) 24, K (C5C7) 20	C5–C7 str. + CO_2 scissors
630	629	S_{29} (99)	W (COO) 99	CO_2 wagging
604	603	S_{10} (78), S_7 (6)	K (N2P4) 59, F (HNP4) 10	N–P str.
520	521	S_{22} (45), S_4 (10)	F (CCO8) 19, H (CCO8) 15	CO_2 rocking + N–C5 str.
408	408	S_{11} (43), S_1 (39)	K (MN) 27, H (HNM) 13	NMCP sym. def. + M–N str.
336	336	S_{31} (73), S_{30} (25)	T (C5N2) 73, T (C5C7) 25	N–C torsion + CO_2 twisting
324	324	S_2 (81), S_1 (9)	K (MO) 71, K (MN) 6	M–O str. + M–N str.
290	291	S_1 (28), S_{11} (14)	K (MN) 19, F (P4NC5) 10	M–N str. + NMCP sym. def.
219	218	S_{30} (74), S_{31} (25)	T (C5C7) 74, T (C5N2) 25	CO_2 twisting + N–C torsion
	211	S_{12} (43), S_{24} (10)	H (P4NC5), F (P4NC5) 23	MNCP deg. def. 1 + MO bending

Table 7. Observed and calculated frequencies related to the metal–ligand bond for A type complexes (cm^{-1})

	Sarcosine				*N*-Phenylglycine				
Vib. mode	Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
NH str.	3243 (3243)*	3247 (3246)	3190 (3190)	3235 (3235)	3234 (3233)	3220 (3220)	3142 (3143)	3227 (3228)	3243 (3242)
CO_2 asym. str.	1602 (1602)	1599 (1599)	1624 (1624)	1604 (1604)	1601 (1602)	1595 (1595)	1616 (1616)	1594 (1592)	1594 (1593)
NH bending 2	1486 (1486)	1489 (1486)	1469 (1469)	1489 (1486)	1490 (1491)	1487 (1484)	1491 (1492)	1490 (1483)	1492 (1492)
CO_2 sym. str.	1410 (1410)	1397 (1391)	1384 (1384)	1395 (1402)	1392 (1386)	1389 (1389)	1385 (1385)	1390 (1390)	1389 (1390)
NH bending 1	1319 (1315)	1318 (1314)	1316 (1317)	1318 (1317)	1258 (1258)	1300 (1297)	1291 (1289)	1252 (1249)	1256 (1257)
CO_2 scissors	738 (737)	731 (730)	743 (741)	726 (726)	768 (737)	764 (739)	760 (734)	765 (740)	767 (739)
CO_2 wagging	617 (619)	620 (618)	626 (624)	625 (624)	628 (629)	630 (629)	637 (634)	628 (629)	626 (629)
CO_2 rocking	491 (515)	512 (514)	496 (518)	512 (511)	515 (520)	520 (521)	518 (522)	516 (518)	511 (518)
M–N str.	420 (421)	444 (442)	461 (465)	442 (443)	410 (406)	408 (408)	402 (402)	405 (406)	409 (410)
M–O str.	304 (304)	314 (314)	322 (325)	313 (314)	308 (308)	324 (324)	300 (300)	319 (320)	296 (301)

*( ): Calculated value.

M–O stretching vibrations, and the values of M–N and M–O stretching force constants increase in the above order for A type complexes with sarcosine. However these trends are not clearly observed for the dihydrates of *N*-phenylglycine complexes except in the cadmium(II) complex, which has 4*d* electrons.

The frequency separations of COO^- antisymmetric and symmetric stretching vibrations are listed in Table 9, together with those of other α-amino acids complexes. This table shows that the frequency separations of sarcosine and *N*-phenylglycine complexes are larger than those of other α-amino acids complexes. Therefore *N*-substituted groups seem to enhance the covalent bond character of a metal–oxygen bond.

Table 8. Values of force constants and F_{dia} related to the metal–ligand bonds

		Sarcosine				*N*-Phenylglycine				
Force constant		Co(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)
K(MN)	mdyn·Å	0.68	0.85	1.02	0.88	0.56	0.56	0.53	0.57	0.67
K(MO)		0.64	0.69	0.78	0.73	0.69	0.79	0.67	0.80	0.80
K(NH)		5.35	5.36	5.16	5.32	5.33	5.28	5.01	5.31	5.36
K(CO9)		6.32	6.30	6.53	6.36	6.32	6.26	6.48	6.23	6.23
K(CO8)		7.42	7.40	7.63	7.46	7.42	7.36	7.58	7.33	7.33
H(HNC4)		0.35	0.35	0.35	0.35	—	—	—	—	—
H(HNP4)		—	—	—	—	0.35	0.35	0.35	0.35	0.35
H(CCO9)		0.43	0.43	0.43	0.43	0.41	0.41	0.41	0.41	0.41
H(CCO8)		0.43	0.43	0.43	0.40	0.41	0.41	0.41	0.39	0.39
H(OCO)		1.06	0.92	0.70	1.06	0.88	0.92	0.80	0.90	0.90
H(HNM)		0.21	0.20	0.22	0.22	0.22	0.23	0.22	0.213	0.217
P(OCO)	mdyn·Å	0.55	0.55	0.56	0.56	0.57	0.57	0.58	0.57	0.57
F_{dia}(NH sym. str.)	mdyn·Å	5.87	5.88	5.68	5.84	5.84	5.79	5.52	5.82	5.87
F_{dia}(CO_2 asym. str.)		7.27	7.25	7.48	7.31	7.31	7.25	7.47	7.22	7.22
F_{dia}(CO_2 sym. str.)		11.31	11.29	11.52	11.35	11.14	11.28	11.50	11.25	11.25
F_{dia}(MN str.)		0.94	1.11	1.28	1.14	0.80	0.80	0.77	0.81	0.91
F_{dia}(NH bending 1)	mdyn·Å	0.59	0.58	0.59	0.60	0.59	0.60	0.59	0.58	0.59
F_{dia}(NH bending 2)		0.80	0.80	0.76	0.80	0.80	0.80	0.80	0.80	0.80

Table 9. The frequency separation of COO^- antisymmetric and symmetric stretching vibrations (cm^{-1})

Ligand	Ni	Co	Cu	Zn	Cd	Reference
glycine	176	162	201	—	—	[21]
alanine	190	180*	223*	215*	173*	[33]
valine	186	—	229*	—	—	[35]
leucine	195*	183*	242*	188*	169*	[32]
serine	175	—	231*	—	—	[1]
sarcosine	202	192	240	209	—	present work
N-phenyl-glycine	206	209	231*	204	205	present work

*Anhydrous compounds.

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