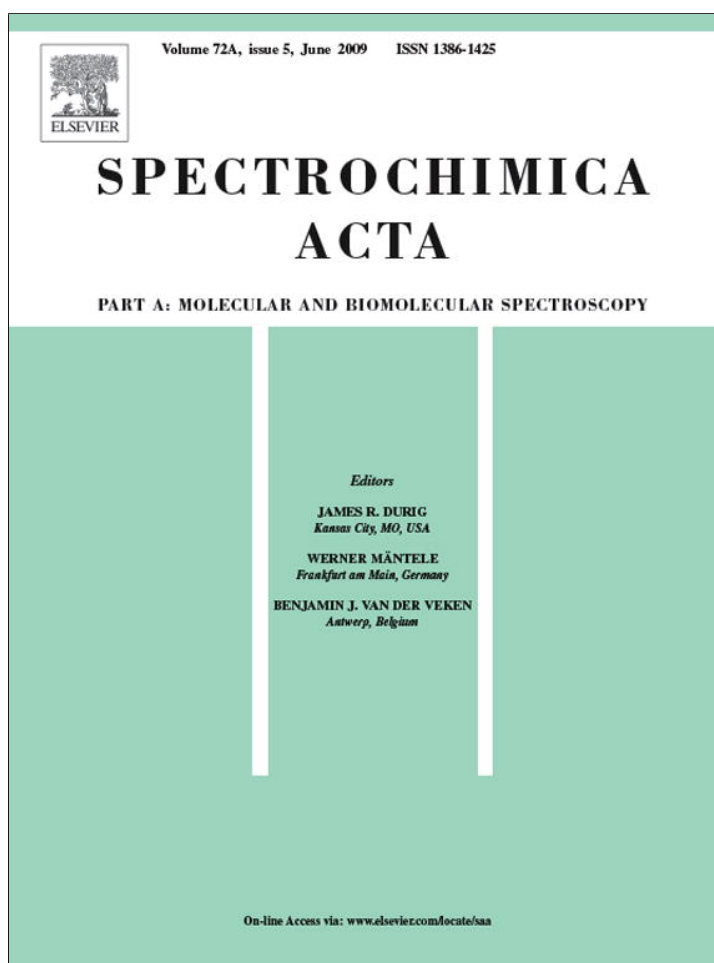


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## Vibrational spectra of Zn(II) complexes of the amino acids with hydrophobic residues

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## ABSTRACT

The infrared and Raman spectra of the bis-chelated Zn(II) complexes of the amino acids glycine, alanine, valine, leucine, isoleucine and phenylalanine were recorded and analyzed in relation to its structural peculiarities. Some comparisons between the recorded spectra are also presented and the characteristics of the carboxylate motions as well as those of the metal-to-ligand vibrations are discussed in detail.

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## 1. Introduction

Zinc is an essential component of an important number of proteins, being indispensable for its stability and/or catalytic function. It is present in over 300 enzymes [1–4] including fundamental enzymatic systems that participate in the formation (polymerases, transferases, and ligases) or degradation (hydrolases) of proteins, nucleic acids, lipids, porphyrins and other important biomolecules, in the stabilization of proteic structures, in control and regulation processes and, even, in the transfer of genetic information [5,6].

The active sites of these enzymes feature a zinc center attached to the protein backbone by three to six amino acid residues, the nature of which influences the specific function of the enzyme. In order to understand why different zinc enzymes use different amino acid residues at the active site, it is necessary to understand how and why the chemistry of zinc is modulated by its coordination environment. Answers to these questions can be provided, partially, by studies of synthetic analogues of these enzymes [4,7], including Zn(II) complexes of amino acids [8].

These zinc complexes can also be used therapeutically in the treatment of anemia, rheumatoid arthritis, wound healing, hepatic disorders and gastric ulcers [9,10] and even for zinc supplementation in the case of zinc deficiencies [9,11,12]. Moreover, zinc complexes also appear as new candidates for the treatment of diabetes [13]. One of the most relevant aspects arising on this context

is the selection of salts or complex compounds, which lead to a rapid and efficient resorption of the metal without upsetting the ionic equilibria in body fluids. Besides, side effects from the ligands and/or ligand components should be negligible or, if possible, therapeutically beneficial. The natural amino acids and derivate small peptides are important candidates for the preparation of such compounds.

During the last years, we have made detailed spectroscopic studies of Cu(II) complexes of amino acids and peptides (cf. [14] and references therein) and have now initiated similar studies with the corresponding Zn(II) complexes. In this paper, we present the first results of these studies, including bis-chelated complexes of the six amino acids containing hydrophobic residues, shown in Fig. 1.

## 2. Experimental

The amino acids (L-form) were purchased from Sigma, all the other used reagents and solvents were analytical grade products. Zn(OH)<sub>2</sub> was obtained, according to the procedure described by Brauer [15]. The investigated complexes were prepared using known synthetic procedures, as follows:

**Zn(gly)<sub>2</sub>·H<sub>2</sub>O:** L-Glycine (0.02 mol) was added to a suspension of ZnO (0.01 mol) in 5 mL of distilled water and strongly mixed in a glass mortar, during 5 min. The obtained mixture was allowed to stand, at room temperature, for 2 days, followed by vacuum drying in an exsiccator [16].

**Zn(ala)<sub>2</sub>:** It was prepared in a similar way as the glycine complex. But in this case the pasty mixture obtained after mixing the reagents was dried for several hours at 80–90 °C [16].

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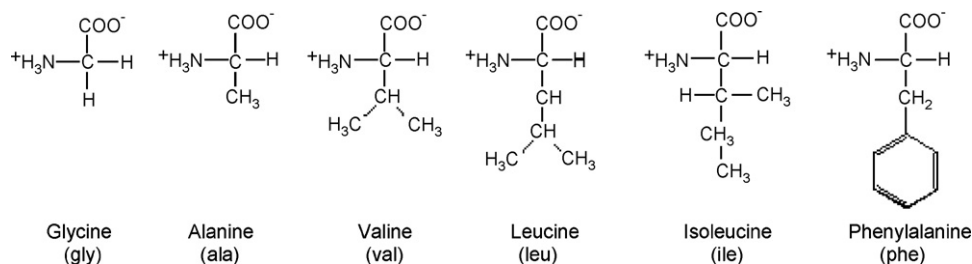


Fig. 1. Schematic structures of the employed amino acids.

$Zn(val)_2 \cdot H_2O$ : A solution of 10 mmol of  $ZnSO_4 \cdot 5H_2O$  in 50 mL of water was slowly added to a 50 mL aqueous solution containing 20 mmol of L-valine and 20 mmol of NaOH at ca. 5 °C (ice-water bath). The solution was warmed up to ambient temperature after 1 h of stirring. The volume of the solution was reduced down to approximately 50 mL by boiling over a water bath. Then, the flask was placed in a temperature-controlled oven at 80 °C. After several days colorless block crystals were obtained [17].

$Zn(leu)_2$ : This complex was obtained in the form of small single crystals using the hydrolysis of urea technique. A solution of 2 mmol of  $ZnCl_2$ , 4 mmol of L-leucine and 2 mmol of urea in 200 mL of distilled water, filtered to eliminate the non-dissolved particles, was maintained at 80 °C in a thermostated bath for 1 week. The crystals were separated from the hot solution by filtration, washed with small portions of water and air-dried [18].

$Zn(ile)_2 \cdot 2H_2O$ : It was prepared in the same way as the glycine complex, but using  $Zn(OH)_2$  instead of ZnO [16].

$Zn(phe)_2$ : A solution of 2 mmol of L-phenylalanine and 1 mL 2 M of NaOH, in 25 mL of distilled water was added dropwise,

under continuous stirring, to a solution containing 2 mmol of o-phenanthroline and 2 mmol of  $Zn(ClO_4)_2 \cdot 6H_2O$  in 25 mL of methanol. After filtration, the solution was left to stand for 1 week. The obtained small crystals were washed first with small portions of methanol, then with water and finally dried in vacuum [8].

The six complexes were characterized by X-ray powder diffraction. The obtained powder diagrams were compared with the theoretical diagrams generated by the program POWDERCELL [19] on the basis of the known single crystal data.

The infrared spectra in the spectral range between 4000 and 250  $cm^{-1}$  were recorded on KBr pellets with a Nicolet Magna 550 FTIR instrument. A total of 32 scans were accumulated. Spectral resolution was  $\pm 4 cm^{-1}$ . Raman spectra, in the same range were obtained with the FRA 106 Raman accessory of a Bruker IFS 66 FTIR instrument. A total of 60 scans were accumulated, using the 1064-nm line of a solid state Nd:YAG laser for excitation. Spectral resolution was  $\pm 4 cm^{-1}$ .

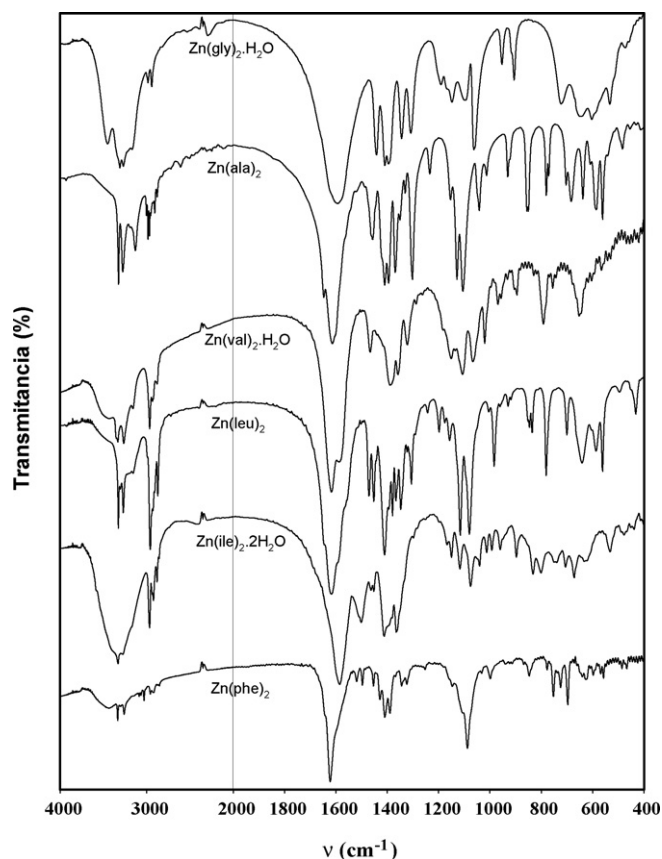


Fig. 2. FTIR spectra of the six investigated Zn(II) complexes.

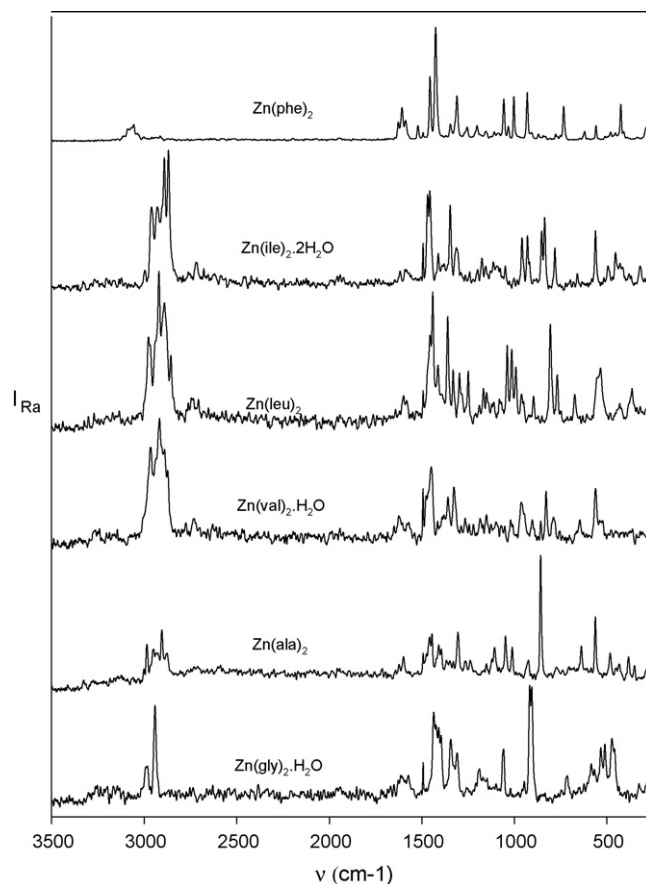


Fig. 3. Raman spectra of the six investigated Zn(II) complexes.

**Table 1**  
Assignment of the most characteristic IR and Raman bands (in  $\text{cm}^{-1}$ ) of  $\text{Zn}(\text{gly})_2 \cdot \text{H}_2\text{O}$  and  $\text{Zn}(\text{ala})_2$ .

$\text{Zn}(\text{gly})_2 \cdot \text{H}_2\text{O}$		$\text{Zn}(\text{ala})_2$		Assignment
IR	Raman	IR	Raman	
3450 s				$\nu(\text{OH})$ lattice water
3308 vs		3323 s	3327 w	
3269 vs	3252 vw	3275 s		$\nu(\text{NH})$
3167 m	3166 vw			
2984 m	2981 m	2984 m	2985 m	
		2966 m	2965 sh	
2940 m	2941 vs	2952 w	2948 m	$\nu(\text{CH})$
		2925 w	2927 m	
		2905 w	2904 m	
1621 sh	1615 m	1647 w	1642 w	$\delta(\text{NH}_2)$ scissor
1593 vs	1574 m	1614 vs	1622 m/1599 m	$\nu_{\text{as}}(\text{COO}^-)$
		1457 m	1457 m/1445 m	$\delta_{\text{as}}(\text{CH}_3)$
1441 s	1435 vs			$\delta(\text{CH}_2)$ scissor
1409 vs	1408 s	1410 s	1408 m	$\nu_{\text{s}}(\text{COO}^-)$
1395 vs	1397 s	1394 s	1395 m	
		1369 w	1368 m	$\delta_{\text{s}}(\text{CH}_3)$
		1351 w/1330 w	1350 m/1330 m	$\delta(\text{CH})$
1344 s	1343 s	1302 s	1304 m	$\delta(\text{CH}_2)$ wagg. + $\nu(\text{C-COO}^-)$
1308 s	1309 m			
1148 m	1148 w	1153 w	1151 w	$\nu(\text{CCN}) + \rho(\text{NH}_2)$
1097 m	1099 w	1128 s	1121 sh	$\delta(\text{NH}_2)$ wagg. + $\nu(\text{C-COO}^-)$
1062 s	1058 m	1042 m	1048 m	$\nu(\text{C-N}) + \rho(\text{NH}_2)$
		1013 w	1012 m	$\rho(\text{CH}_3)$
953 m	947 w			$\rho(\text{CH}_2)$
906 m	917 vs/905 vs	931 m	924 m	$\nu(\text{C-C})$
		856 m/851 m	858 vs	$\nu(\text{CCN})$
		780 m/771 m	775 w/739 w	$\rho(\text{NH}_2) + \rho(\text{COO}^-)$
646 s	647 vw			$\rho(\text{NH}_2) + \rho(\text{COO}^-)$
603 s	584 m	609 w		$\delta(\text{COO}^-)$
533 s	532 m/511 m	542 w		$\rho(\text{COO}^-)$
473 w	472 m	455 w	450 w	$\nu(\text{Zn-N}) + \delta(\text{COO}^-)$
330 w	327 w	352 m	351 m	$\nu(\text{Zn-O})$

vs: very strong; s: strong; m: medium; w: weak; and sh: shoulder.

**Table 2**  
Assignment of the most characteristic IR and Raman bands (in  $\text{cm}^{-1}$ ) of  $\text{Zn}(\text{leu})_2$  and  $\text{Zn}(\text{phe})_2$ .

$\text{Zn}(\text{leu})_2$		$\text{Zn}(\text{phe})_2$		Assignment
IR	Raman	IR	Raman	
3326 s/3269 s		3333 m/3253 m		$\nu(\text{NH})$
	2995 m			
2958 s	2960 s	2960 w		
2927 sh	2927 s			$\nu(\text{CH})$
2907 sh	2891 vs	2912 w		
2870 m	2869 vs			
1617 vs	1618 w	1623 vs	1626 m	$\delta(\text{NH}_2)$ scissor
1617 vs	1592 w	1587 sh	1588 m	$\nu_{\text{as}}(\text{COO}^-)$
1471 s/1452 s	1468 s/1456 s			$\delta_{\text{as}}(\text{CH}_3)$
1410 s	1411 m	1428 s	1425 vs	$\delta(\text{CH}_2)$ scissor
1394 sh	1388 w	1409 s/1389 s	1387 w	$\nu_{\text{s}}(\text{COO}^-)$
1366 s				$\delta_{\text{s}}(\text{CH}_3)$
1347 s	1346 s			$\delta(\text{CH})$
		1343 m	1345 m	$\delta(\text{CH})$
1323 w	1314 m	1324 w	1311 s	$\delta(\text{CH}_2)$ wagg. + $\nu(\text{C-COO}^-)$
1306 m				
1291 sh/1243 w	1264 w/1242 w	1254 w/1226 w	1256 m	$\delta(\text{CH}_2)$
1157 m	1154 w	1147 m	1154 w	$\nu(\text{CCN}) + \rho(\text{NH}_2)$
1115 s	1114 m	1107 sh	1107 w	$\delta(\text{NH}_2)$ wagg. + $\nu(\text{C-COO}^-)$
1080 s	1076 w/1048 m	1088 vs	1086 w/1057 s	$\nu(\text{C-N}) + \rho(\text{NH}_2)$
1004 w	1002 w			$\rho(\text{CH}_3)$
		997 m	1002 s	$\rho(\text{CH}_2)$
961 vw	959 m	939 w/931 w	931 s	$\nu(\text{C-C})$
		914 w	907 w	
846 m/836 m	853 m/836 s	868 m/847 s	869 w	$\nu(\text{CCN})$
781 s	781 m	776 m/754 s	777 w	$\rho(\text{NH}_2) + \rho(\text{COO}^-)$
641 s	660 m	643 m/623 s	621 m	$\rho(\text{NH}_2) + \rho(\text{COO}^-)$
587 m	582 w	597 w		$\delta(\text{COO}^-)$
		558 w	559 m	$\rho(\text{COO}^-)$
495 w	495 m	424 w	426 s	$\nu(\text{Zn-N}) + \delta(\text{COO}^-)$
382 w	381 w	341 w	335 w	$\nu(\text{Zn-O})$

vs: very strong; s: strong; m: medium; w: weak; and sh: shoulder.

**Table 3**Assignment of the most characteristic IR and Raman bands (in  $\text{cm}^{-1}$ ) of  $\text{Zn}(\text{val})_2 \cdot \text{H}_2\text{O}$  and  $\text{Zn}(\text{ile})_2 \cdot 2\text{H}_2\text{O}$ .

$\text{Zn}(\text{val})_2 \cdot \text{H}_2\text{O}$		$\text{Zn}(\text{ile})_2 \cdot 2\text{H}_2\text{O}$		Assignment
IR	Raman	IR	Raman	
3331 m/3263 m	3262 w	3330 vs/3273 w		$\nu(\text{NH})$
2963 m	2965 s	2964 s	2976 s	
2932 w	2917 vs	2937 sh		
2877 w	2889 s	2920 m	2918 vs	$\nu(\text{CH})$
	2873 s	2879 m	2890 vs	
		2856 w	2855 m	
1617 vs	1624 m	1585 vs	1597 m	$\delta(\text{NH}_2)$ scissor
1582 sh	1569 m	1585 vs	1582 m	$\nu_{\text{as}}(\text{COO}^-)$
1467 m	1477 sh/1450 s	1463 m/1452 m	1456 s/1441 vs	$\delta_{\text{as}}(\text{CH}_3)$
1389 m	1380 m	1412 vs	1412 m	$\nu_s(\text{COO}^-)$
1358 m	1358 s	1364 s	1360 vs	$\delta_s(\text{CH}_3)$
1322 m	1326 s			$\delta(\text{CH})$
		1298 sh	1296 m	$\delta(\text{CH}_2)$ wagg. + $\nu(\text{C}-\text{COO}^-)$
1151 m	1150 w	1150 m	1150 m	$\nu(\text{CCN}) + \rho(\text{NH}_2)$
1107 m	1098 w	1117 m	1110 w	$\delta(\text{NH}_2)$ wagg. + $\nu(\text{C}-\text{COO}^-)$
1067 m	1071 w	1040 m	1039 s	$\nu(\text{C}-\text{N}) + \rho(\text{NH}_2)$
1020 m	1020 w	1013 m	1015 s	$\rho(\text{CH}_3)$
969 m/957 w	964 m	960 m	962 m	$\nu(\text{C}-\text{C})$
930 w	946 sh			
895 m	903 m	832/801 m	806 s	$\nu(\text{CCN})$
792 m	789 m	750/745 w	768 m	$\rho(\text{NH}_2) + \rho(\text{COO}^-)$
		672 m	674 m	$\rho(\text{NH}_2) + \rho(\text{COO}^-)$
617 w/604 w				$\delta(\text{COO}^-)$
542 w	539 m	569 vw	552 sh	$\rho(\text{COO}^-)$
		532 m	534 m	$\rho(\text{H}_2\text{O})$ (?)
423 w		478 m/439 w	431 w	$\nu(\text{Zn}-\text{N}) + \delta(\text{COO}^-)$
374 w	362 w	375 m	365 m	$\nu(\text{Zn}-\text{O})$

vs: very strong; s: strong; m: medium; w: weak; and sh: shoulder.

### 3. Results and discussion

#### 3.1. Structural characteristics of the complexes

Structural information is available for all of the investigated compounds. All amino acids act as bidentate ligands, through one O-atom of the carboxylate group and the N-atom of the amino moiety. The most relevant aspects are summarized, as follows:

$\text{Zn}(\text{gly})_2 \cdot \text{H}_2\text{O}$ : Triclinic, space group  $P(-1)$ ,  $Z=4$ . Amino acid arrangement: *trans*. Zn-environment:  $\text{ZnN}_2\text{O}_2\text{O}'$ , approximately square pyramidal with a significant distortion ( $\text{O}'$  is a carboxyl atom from a neighboring  $\text{Zn}(\text{gly})_2$  complex) [20].

$\text{Zn}(\text{ala})_2$ : Monoclinic, space group  $P2_1$ ,  $Z=2$ . Amino acid arrangement: *trans*. Zn-environment:  $\text{ZnN}_2\text{O}_2\text{O}'$ , approximately square pyramidal ( $\text{O}'$  is a carboxyl atom from a neighboring complex) [21].

$\text{Zn}(\text{val})_2 \cdot \text{H}_2\text{O}$ : Orthorhombic, space group  $P2_12_12_1$ ,  $Z=4$ . Amino acid arrangement: *cis*. Zn-environment:  $\text{ZnN}_2\text{O}_2\text{O}'$ , distorted square pyramidal ( $\text{O}'$  atom from a water molecule) [17].

$\text{Zn}(\text{leu})_2$ : Monoclinic, space group  $P2_1$ ,  $Z=2$ . Amino acid arrangement: *trans*. Zn-environment:  $\text{ZnN}_2\text{O}_2\text{O}'$ , squashed tetrahedral ( $\text{O}'$  is a carboxyl atom from a neighboring  $\text{Zn}(\text{leu})_2$  complex) [18].

$\text{Zn}(\text{ile})_2 \cdot 2\text{H}_2\text{O}$ : Monoclinic, space group  $C2$ ,  $Z=2$ . Amino acid arrangement: *trans* for N and *cis* for O. Zn-environment:  $\text{ZnN}_2\text{O}_2\text{O}'\text{O}''$ , approximately octahedral ( $\text{O}'$  and  $\text{O}''$  atoms from water molecules) [8].

$\text{Zn}(\text{phe})_2$ : Monoclinic, space group  $P2_1$ ,  $Z=4$ . Amino acid arrangement: *trans*. Zn-environment:  $\text{ZnN}_2\text{O}_2\text{O}'$ , distorted trigonal bipyramidal ( $\text{O}'$  is a carboxyl atom from a neighboring complex) [8].

#### 3.2. Infrared and Raman spectra

The spectra of all the investigated compounds are very complex presenting a great number of bands in all spectral ranges. Therefore, it seems very difficult to attempt a detailed assignment of them. Notwithstanding, the most important and characteristic vibrational modes could be identified and comparisons between all

the investigated compounds could be made, allowing some general conclusions on their vibrational behavior.

The spectra of the six investigated complexes are shown in Figs. 2 and 3, and as it can be seen, they present very similar spectral patterns, pointing clearly to very similar coordination characteristics in all of them. The proposed spectral assignments are presented in Tables 1–3, grouped according to specific characteristics:  $\text{Zn}(\text{gly})_2 \cdot \text{H}_2\text{O}$  and  $\text{Zn}(\text{ala})_2$  present the same distorted square pyramidal environment, with the fifth position occupied by an O(carboxyl) atom from a neighboring amino acid molecule.  $\text{Zn}(\text{leu})_2$  and  $\text{Zn}(\text{phe})_2$  show distorted trigonal bipyramidal environments and  $\text{Zn}(\text{val})_2 \cdot \text{H}_2\text{O}$  and  $\text{Zn}(\text{ile})_2 \cdot 2\text{H}_2\text{O}$ , although of different structures, present one or two water molecules bonded to the metal center.

The assignments have been performed on the basis of previous studies [14,22–25] and with the aid of some standard references [26–28]. Most of the characteristic bands related to CH,  $\text{CH}_2$  and  $\text{CH}_3$  deformational modes, and other skeletal vibrations appear at very similar energies in all the spectra. In the higher frequency region our assignment has not differentiated the stretching vibrations related to these different groupings and the range between 2984 and 2850  $\text{cm}^{-1}$  was generically identified as  $\nu(\text{CH})$ .

The vibrations of the water molecules present in the glycine, valine and isoleucine complexes could only be identified in the first species, in which water is present as lattice water. In the other two cases, the O–H stretching modes are overlapped by the strong and broad amino stretchings whereas the  $\delta(\text{H}_2\text{O})$  vibration is surely overlapped by the strong  $\nu_{\text{as}}(\text{COO}^-)$  vibration. In the case of  $\text{Zn}(\text{ile})_2 \cdot 2\text{H}_2\text{O}$  one of the librational modes of coordinated water could be tentatively assigned. On the other hand, the typical  $\text{NH}_2$ -scissoring mode is also superimposed with the  $\nu_{\text{as}}(\text{COO}^-)$  band in the case of the leucine and isoleucine complexes.

One particularly interesting aspect to be analyzed in complexes of this type is the displacement of the characteristic carboxylic bands after coordination. This peculiar aspect has been summarized in Table 4. The “free” amino acids exists as zwitterions in the

**Table 4**  
Comparisons of the carboxylate vibrations (in  $\text{cm}^{-1}$ ) in the “free” amino acids and in its Zn(II) complexes.

	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$
Glycine	1608	1412
Zn(gly) <sub>2</sub> ·H <sub>2</sub> O	1593	1409/1395
Alanine	1605	1413
Zn(ala) <sub>2</sub>	1614	1410/1394
Valine	1586	1425
Zn(val) <sub>2</sub> ·H <sub>2</sub> O	1582	1389
Leucine	1583	1407
Zn(leu) <sub>2</sub>	1617	1394/1379
Isoleucine	1602	1418
Zn(ile) <sub>2</sub> ·2H <sub>2</sub> O	1585	1412
Phenylalanine	1564	1411
Zn(phe) <sub>2</sub>	1581	1369

crystalline state; thus, one expects two stretching vibrations for the  $\text{COO}^-$  moiety present in these systems, namely  $\nu_{\text{s}}(\text{COO}^-)$  and  $\nu_{\text{as}}(\text{COO}^-)$ . The first one is usually of medium intensity in the IR spectrum, whereas the second is strong and broad. After coordination, one should expect a lowering of the frequency of one of these bands, due to the generation of a Zn–O bond and the energy increase of the other, because the C–O double bond is partially reconstructed.

Nevertheless, as it can be seen from the data presented in Table 4, the band which is assigned to the  $\nu_{\text{s}}(\text{COO}^-)$  stretching in the “free” acid suffers a small shift to lower frequencies in all cases, as expected. However, interestingly, the other vibration is not always displaced to higher wavenumbers after complex formation. In fact, it also suffers a small energy decrease in three of the complexes, whereas in the other three only a rather small increment can be observed. This behavior can be explained by the fact that

this not coordinated C=O group participated in hydrogen bonding with water molecules or is involved in weak secondary bonds to the metal center of a neighboring complex. Both interactions produce, obviously, a weakening of this partially reconstructed C=O bond [26].

Another aspect which should be especially emphasized are the positions of the Zn–N and Zn–O metal-to-ligand vibrations. The identification of bands related to these modes, comparing the spectra of the complexes with those of the free ligands, is not always easy because most of the amino acids present a great number of bands in the spectral region in which this vibrations are expected. This important part of the spectra is depicted schematically in Fig. 4.

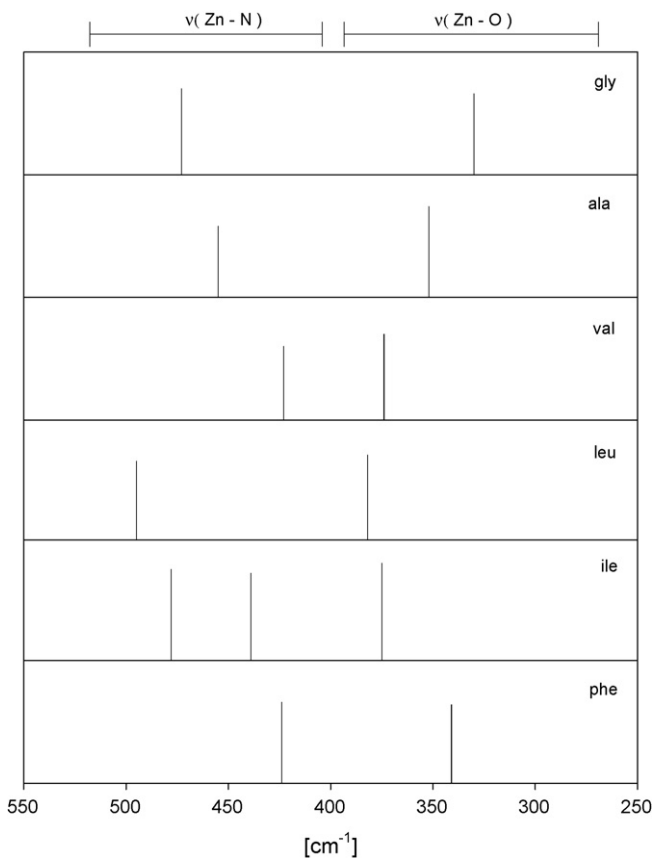
In the case of the *cis*-isomer Zn(ile)<sub>2</sub>·2H<sub>2</sub>O, two Zn–N vibrations are observed, whereas for the remaining *trans*-isomers only one band for each of the two modes is observed, as expected [22,28]. As it can also be seen from Fig. 4 all these vibrations are found in very similar spectral ranges, in agreement with the fact that all Zn–N and Zn–O bond lengths are very similar. Besides, this metal-to-ligand vibrations appear in very similar ranges as for the related bis-chelated Cu(II) complexes of the same amino acids [22].

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**Fig. 4.** Schematic representation of the positions of the metal-to-ligand vibrations of the investigated complexes.