Acta Farm. Bonaerense **19** (3): 231-4 (2000)
Recibido el 10 de marzo de 2000
Aceptado el 15 de julio de 2000

Vibrational Spectra of the Cu(II) Complexes of Aspartic and Glutamic Acids

Enrique J. BARAN [1]*, Claudia C.WAGNER [1], María H.TORRE [2],
Eduardo KREMER [2] and Paul KÖGERLER [3]

[1] *Centro de Química Inorgánica (CEQUINOR;CONICET/UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.Correo 962, 1900 La Plata, Argentina.*
[2] *Química Inorgánica, Facultad de Química, Universidad de la República, Montevideo, Uruguay.*
[3] *Lehrstuhl für Anorganische Chemie I, Fakultät fur Chemie, Universität Bielefeld, D-33501 Bielefeld, Germany.*

SUMMARY. The infrared and Raman spectra of Cu(asp).$2H_2O$ and Cu(glu).$2H_2O$ (asp = L-aspartate; glu = L-glutamate) were recorded and discussed in relation to their crystal structures. Some comparisons with Cu(II) complexes of other amino acids are also made.

RESUMEN. "Espectros Vibracionales de los Complejos de Cu(II) con los Acidos Aspártico y Glutámico". Se registraron los espectros infrarrojos y Raman de los complejos Cu(asp).$2H_2O$ y Cu(glu). $2H_2O$ (asp = L-aspartato; glu = L-glutamato) y se los discute en base a sus estructuras cristalinas. Se realizan algunas comparaciones con otros complejos de Cu(II) con amino ácidos.

INTRODUCTION

As a part of a research project devoted to the synthesis and characterization of copper complexes with pharmacological activity, we are investigating some general physicochemical properties of Cu(II) complexes of α-amino acids. As it is well known, many of these complexes possess an effective anti-rheumatic and/or anti-inflammatory activity [1-5]. In previous papers we have investigated the vibrational spectra of the complexes derived from amino acids containing hydrophobic [6] and hydroxylic [7] residues.

We have now extended these studies to the two acidic α-amino acids present in almost all proteins, i.e., L-aspartic and L-glutamic acid. Both complexes present the same stoichiometry, i.e., Cu(aa). $2H_2O$.

Cu(glu).$2H_2O$ is orthorhombic, space group $P2_12_12_1$ and Z = 4. The coordination about the copper ions is approximately square planar, involving the N atom and one α-carboxylate oxygen atom of one glutamate moiety, a β-carboxylate oxygen of another amino acid group and the oxygen atom of one of the water molecules. The Cu-O and Cu-N distances range from 1.97 to 2.00 Å. Two additional glutamate oxygen atoms at 2.30 and 2.59 Å complete a severely distorted octahedron [8].

Cu(asp). $2H_2O$ crystallizes in the monoclinic space group C2 with Z = 4. The coordination of the Cu(II) cation is a distorted tetragonal pyramid. The shortest equatorial bonds occur at the base of the pyramid with a water oxygen, the nitrogen atom and an α-carboxylate oxygen of one aspartate ion and a β-carboxylate oxygen of another aspartate ion. The oxygen atom of the second water molecule occupies the apical position [9].

EXPERIMENTAL

(L-aspartato)diaquacopper(II), Cu(Asp).$2H_2O$, was obtained by mixing hot aqueous solutions of copper(II) acetate and L-aspartic acid and digesting the generated precipitate at 50 °C during one hour [10]. The similar complex of L-glutamic acid, Cu(Glu).$2H_2O$, was prepared in a similar way using copper(II) nitrate [8]. The composition of both complexes was confirmed by elemental chemical analysis.

The IR spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr pellet technique. Raman spectra were obtained with a Bruker IFS 66 FTIR instrument provided with a FRA 106 Raman accessory. The samples were excited with the 1064 nm line of a Nd: YAG laser.

KEY WORDS: Cu(II) complexes, Aspartic Acid, Glutamic Acid, IR and Raman Spectra.
PALABRAS CLAVE: Complejos de Cu(II), Acido Aspártico, Acido Glutámico, Espectros IR y Raman.

* Author for correspondence

RESULTS AND DISCUSSION

The spectra of the investigated compounds are very complex and present a great number of bands in all the spectral ranges. Notwithstanding, the most important and characteristic bands could be clearly identified and an approximate assignment for some others could be given on the basis of our previous results [6,7] and with the aid of some general reference data [11-13].

The infrared and Raman spectra of Cu(asp). $2H_2O$ in the spectral range between 1800 and 200 cm^{-1} are shown in Figures 1 and 2, respectively. The proposed assignment of the complete spectra is presented in Table 1. Similarly, spectra for the glutamato complex are shown in Figures 3 and 4, whereas the corresponding assignment is given in Table 2.

Some general comments on the obtained results and proposed assignments are presented below:

- For the Cu(asp). $2H_2O$ the O-H stretching vibrations are clearly separated from the respective N-H motions, in agreement with the presence of long and medium hydrogen bonds, involving the water molecules and the amino groups [9,14]. These hydrogen bond interactions are slightly shorter in the glutamato complex [8], shifting the ν(OH) bands to lower wavenumbers. Therefore, in this case these stretchings cannot be clearly distinguished from the ν(NH) bands.

- For this last mentioned vibration, the ν_{as}(NH) and ν_s(NH) components can be differentiated in the infrared spectrum (3324 and 3268 cm^{-1}, respectively, in the asparatato complex; 3317 and 3218 cm^{-1}, respectively, in the glutamato complex) (*cf.* also refer. [15]). Interestingly, only very weak Raman lines are found in this region.

- The C-H and CH_2 stretching vibrations are seen as very intense lines in the Raman spectra and are practically absent in the corresponding infrared spectra. A greater number of lines is seen in the case of Cu(glu). $2H_2O$ in agreement with the presence of an additional CH_2 group in this ligand.

- In both complexes the ν(C=O) band is clearly splitted, in agreement with the existence of two structurally non-equivalent carboxylate groups. The bending mode of the water molecules, which are expected to lie in the same range [14] are surely overlapped by this very strong stretching bands. Also for the ν(C-O) mode two bands are observed in both complex-

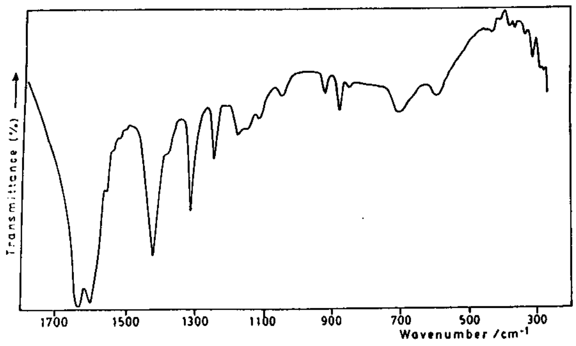

Figure 1. Infrared spectrum of Cu(asp).$2H_2O$.

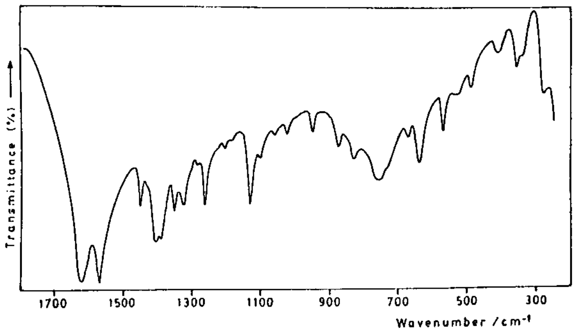

Figure 3. Infrared spectrum of Cu(glu).$2H_2O$.

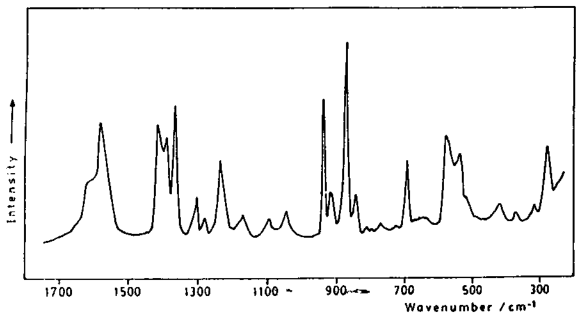

Figure 2. Raman spectrum of Cu(asp).$2H_2O$.

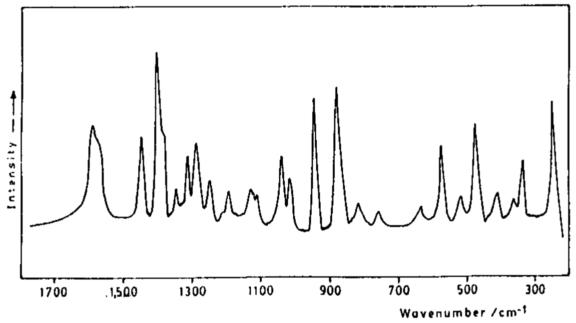

Figure 4. Raman spectrum of Cu(glu).$2H_2O$.

Infrared^a (ν /cm^{-1})	**Raman (ν /cm^{-1})**	**Assignment**
3489 vs,br	- - - -	ν (OH)
3324 sh, 3268 s	3247 w	ν (NH)
- - - -	2989s, 2966s, 2939vs	ν (CH)
1629 vs, 1592 vs	1630 m, 1581 s	ν (C=O)
1410 vs	1416 s, 1395 m	ν (C-O)
1368 w	1369 s	ν (C-CO_2)
1300 vs	1302 m, 1279 w	CH_2 -wagg.
1231 m	1234 m	τ (CH_2) + ν (C-C)
1164 m	1167 w	τ (NH_2) + ν (C-C)
1136 m	- - - -	(NH_2)-wagg.+ν(C-CO2)
1098 w	1098 w	ν (CN)
1034 w	1040 w, 940 s	CH_2 -rock + ν (C-C)
909 m	910 w	CO_2 -sciss.
864 m	867 vs	ρ (H_2O)
837 w	837 w	
688 m,br	695 m	(NH_2)-rock+(CO_2)-rock
570 m,br	573 s, 537 m	
415 w	416 w	ν (Cu-N)
366 w, 350 w	360 vw	ν (Cu-O)
320 w	320 w	ν (Cu-O)
297 m	293 s	

Table 1. Assignment of the vibrational spectrum of Cu(asp).$2H_2O$ ^{a} vs, very strong; s, strong; m, medium; w, weak, vw, very weak; sh, shoulder; br, broad.

Infrared ^{a} (ν /cm^{-1})	**Raman (ν /cm^{-1})**	**Assignment**
3317 s, 3218 s,br	3312 w, 3245 w	ν (NH) + ν (OH)
2965 vw	3016 m, 2976 vs	ν (CH)
2931 vw	2932 vs, 2913 vs	ν (CH)
1626 vs, 1573 vs	1596 s, 1580 sh	ν (C=O)
1454 m	1454 s	CH_2-scissor
1407s, 1392s	1408vs,1390sh	ν (C-O)
1354 m, 1327 m	1356 w, 1325 m	ν (C-CO_2)
1266 s	1288 m, 1260 w	CH_2 -wagg.
1206 w, 1190 vw	1191 w	τ (CH_2) + ν (C-C)
1134 s, 1105 w	1135 w, 1106 w	(NH_2)-wagg.+ν (C-CO_2)
1062 w, 1025 w	1065 m, 1026 s	ν(CN)
951 m	950 s	
875 m	876 vs	ρ (H_2O)
830 m	830 w	ρ (H_2O)
761 s,br, 669 w	760 vw, 676 vw	(NH_2)-rock+(CO_2)-rock
635 s, 568 m, 526 w	633 w, 573 s, 520 w	
485 m	486 s	ν (Cu-N)
410 m	412 w	
353s, 335 w	350 w, 341 m	ν (Cu-O)
247 s	251 s	

Table 2. Assignment of the vibrational spectrum of Cu(glu).$2H_2O$ ^{a} vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

Acid/Complex	**$\nu_{as}(COO^-)$**	**$\nu_s(COO^-)$**
L-aspartic acid	1592 s, 1550 m	1418 vs
Cu(asp).$2H_2O$	1629 vs,1592 vs	1410 vs
L-glutamic acid	1662 m, 1644 s	1434 w, 1419 s
Cu(glu).$2H_2O$	1626 vs, 1573 vs	1407 s, 1392 s

Table 3. Comparison of the typical carboxylate stretching bands of the the free amino acids and the respective Cu(II) complexes (infrared data, values in cm^{-1}); vs, very strong; s, strong; m, medium.

es, except in the infrared spectrum of Cu(asp).$2H_2O$, which only shows one band in this region.

- The band assigned to the ρ(H_2O) in the aspartato complex is very strong in the Raman spectrum and presents medium intensity in the infrared. In the glutamato complex two bands of this type could be identified, in agreement with the presence of two coordinated water molecules in this case. But, interestingly, In this last case only one of these bands, that located at higher wavenumbers, shows a high Raman intensity.

- The positions of the ligand-to-metal vibrations were obtained by comparison of the complex spectra with those of the corresponding free ligands and with results of the previously investigated systems [6,7] (*cf.* also refer. [16]). These bands are found in similar ranges as for these other complexes. In the case of Cu(asp). $2H_2O$ three bands related to ν(Cu-O) vibrations are found in agreement with the existence of more Cu-O bonds in this complex. Those at the lowest energy (320 cm^{-1}) can probably be assigned to the Cu-O bond involving the apical water molecule.

Finally, we have analyzed the displacement of the characteristic carboxylic bands after their bonding to the metallic center. The "free" amino acids exist as zwitterions in the crystalline state; thus one expects two vibrations for the COO^- moieties present in these systems ($\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively). After coordination an energy lowering of one of these bands is expected, due to the generation of the Cu-O bond and the increase of the other one, because a C-O double bond is partially reconstructed. As it can be seen from the data presented in Table 3, the bands assigned to the $\nu_s(COO^-)$ vibration in the "free" acid suffer a small shift to lower wavenumbers in both cases, in agreement with the participation of the C-O bonds in binding. Interestingly, however, the other band is not always reinforced after complex formation. In most of the previously investigated Cu(II) complexes of amino acids [6,7], this band also suffers a small frequency decrease after complex formation. This behaviour could be explained by the fact that this C=O group often participates in hydrogen bonding with water molecules or is involved in weak secondary bonds to the metal centers. This is the situation for the Cu(glu).$2H_2O$ complex in which these C=O bonds participate in the formation of the two longer Cu-O bonds which complete the distorted octahedral coordination around Cu(II) [8]. On the other hand, such secondary bonds are not established in the case of the aspartato complex [9], and therefore in this case the expected trends are observed.

Acknowledgements. This work was supported by the "Consejo Nacional de Investigaciones Científicas y Tecnológicas de la República Argentina" (CONICET) and by the Agencia Nacional de Promoción Científica y Tecnológica (Préstamo BID 802/OC-AR-PICT Nr.119). C.C.W. benefits from a research fellowship from FOMEC and E.J.B. is a member of the Research Career from CONICET.

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