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## Vibrational and electronic spectra of $[\text{Cu}(\text{L-ornithinato})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$

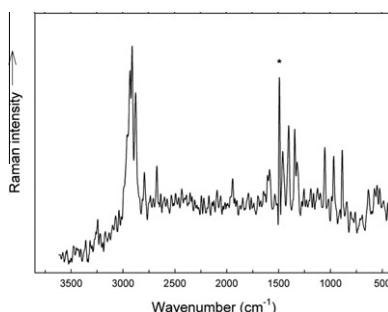
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### HIGHLIGHTS

- ▶ FTIR and FT-Raman spectra of  $[\text{Cu}(\text{L-ornithinato})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  were recorded.
- ▶ Spectra were assigned on the basis of the known crystal structure.
- ▶ Electronic spectra were also recorded and briefly discussed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The FTIR and FT-Raman spectra of a Cu(II) complex of ornithine of composition  $[\text{Cu}(\text{L-ornithinato})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  were recorded and analyzed in relation to its structural peculiarities and by comparison with the spectra of ornithine hydrochloride and of other *bis*(amino acid) complexes of Cu(II). The electronic spectrum of the complex is also briefly discussed.

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### Introduction

Besides iron and zinc, copper is the most ubiquitous transition metal present in living organisms and is involved in a large number of important functions and processes. Copper metalloenzymes are present in oxidases (laccases, ascorbate oxidase, galactose oxidase, amine oxidases), participate in oxygenation and dismutation reactions (plastocyanins, tyrosinases, superoxide dismutases) and even in oxygen transport in arthropods and mollusks (hemocyanins) [1–5].

On the other hand, numerous copper compounds and, in particular, Cu(II) complexes present relevant pharmacological interest as

several of them show an important number of effects, including anti-inflammatory, antiulcer, anticonvulsant and anti-tumoral activity [6–10]. In this context, copper complexes of most of the simplest amino acids showed a particular relevance, appearing even useful for copper supplementation in human and veterinary medicine [9,11].

Due to the commented importance of these complexes we have repeatedly investigated their structural and general physicochemical properties since the last ten years. As an extension of these studies we have now investigated the spectroscopic behavior of the simple Cu(II)/ornithinato complex of stoichiometry  $[\text{Cu}(\text{L-ornithinato})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ . Although ornithine (Fig. 1) is one of the amino acids which are not found in proteins, it plays a key function in the urea cycle [12].

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## Experimental

The starting materials for the synthesis of the complex were L-ornithine monohydrochloride (Fluka) and  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (Mallinckrodt), which were used as supplied. The complex was obtained by interaction of L-ornithine monohydrochloride (2.00 g, 12 mmol) with a slight excess of  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  suspended in 50 mL of distilled water. The mixture was heated and stirred over a water bath for one hour and then the excess of basic carbonate was removed by filtration and the resulting limpid dark blue solution was concentrated to half its volume over a water bath and then left to evaporate in air. When almost all the solvent was evaporated, a blue compact solid was deposited. It was filtered off and dried in air during a few days.

Elemental chemical analysis, performed on a Carlo Erba model EA 1108 elemental analyzer, confirmed the stoichiometry  $[\text{Cu}(\text{L-orn})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  (Exper.: C = 27.45%; H = 6.55%; N = 12.65%. Calc. for  $\text{C}_{10}\text{H}_{28}\text{O}_6\text{N}_4\text{Cl}_2\text{Cu}$  (MW = 434.44): C = 27.62%; H = 6.44%; N = 12.89%).

Infrared spectra were recorded with a FTIR-Bruker Equinox-55 instrument, using the KBr pellet technique. Raman spectra were obtained with the FRA 106 accessory of a Bruker IFS66 FTIR spectrophotometer, using the 1064 nm radiation from a Nd:YAG laser for excitation. Spectral resolution was  $\pm 4 \text{ cm}^{-1}$  in both spectral measurements.

The electronic absorption spectra were measured with a Hewlett-Packard 8452 diode-array spectrophotometer, using 10 mm quartz cells.

## Results and discussion

### Structural characteristics of $[\text{Cu}(\text{L-orn})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$

The crystal structure of the complex was determined some years ago by Guha and Saha [13]. It crystallizes in the monoclinic  $P2_1/c$  space group and  $Z=2$ , with  $a=5.18$ ,  $b=15.57$  and  $c=11.90 \text{ \AA}$  and  $\beta=93.3^\circ$ . The crystal structure is similar in many ways to those of other Cu(II) complexes of amino acids, whose structures are known. The molecule shows a distorted octahedral geometry around the metal center, with two pairs of oxygen and nitrogen atoms, provided by the carboxylate and  $\alpha$ -amino groups, forming an approximately square planar coordination (bonding distances:  $\text{Cu-N}=1.992(6) \text{ \AA}$  and  $\text{Cu-O}=1.976(5) \text{ \AA}$ ). The octahedron is completed with two chloride ions occupying the apical positions ( $d(\text{Cu-Cl})=2.891(2) \text{ \AA}$ ). The terminal  $\omega$ - $\text{NH}_2$  groups remain protonated. The water molecules are present as crystal water and participate in the hydrogen bonding network that stabilizes the structure [13].

A closely related structure is that of  $[\text{Cu}(\text{L-lysinato})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  (also monoclinic, space group  $P2_1$  and  $Z=2$ , with  $a=5.189$ ,  $b=16.988$ , and  $c=11.482 \text{ \AA}$  and  $\beta=93.57^\circ$ ) [14], because L-ornithine and L-lysine differ only from one another for the length of the spacer ( $n$  = methylene residues) between the  $\omega$ - $\text{NH}_2$  terminal and  $\alpha$ - $\text{NH}_2$  group:  $n=3$  for ornithine (cf. Fig. 1) and  $n=4$  for lysine. In this L-lysinato complex the coordination sphere of the Cu(II) cation is the same as described above for L-ornithine.

### Infrared and Raman spectra

The FTIR and FT-Raman spectra of  $[\text{Cu}(\text{L-orn})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  are shown in Fig. 2 and the proposed assignment is presented in Table 1. It is based on some standard references [15,16], as well as on some recent studies of L-ornithine monohydrochloride [17,18] and on the recently investigated, and closely related,  $[\text{Cu}(\text{L-lys})_2$

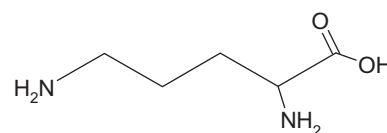
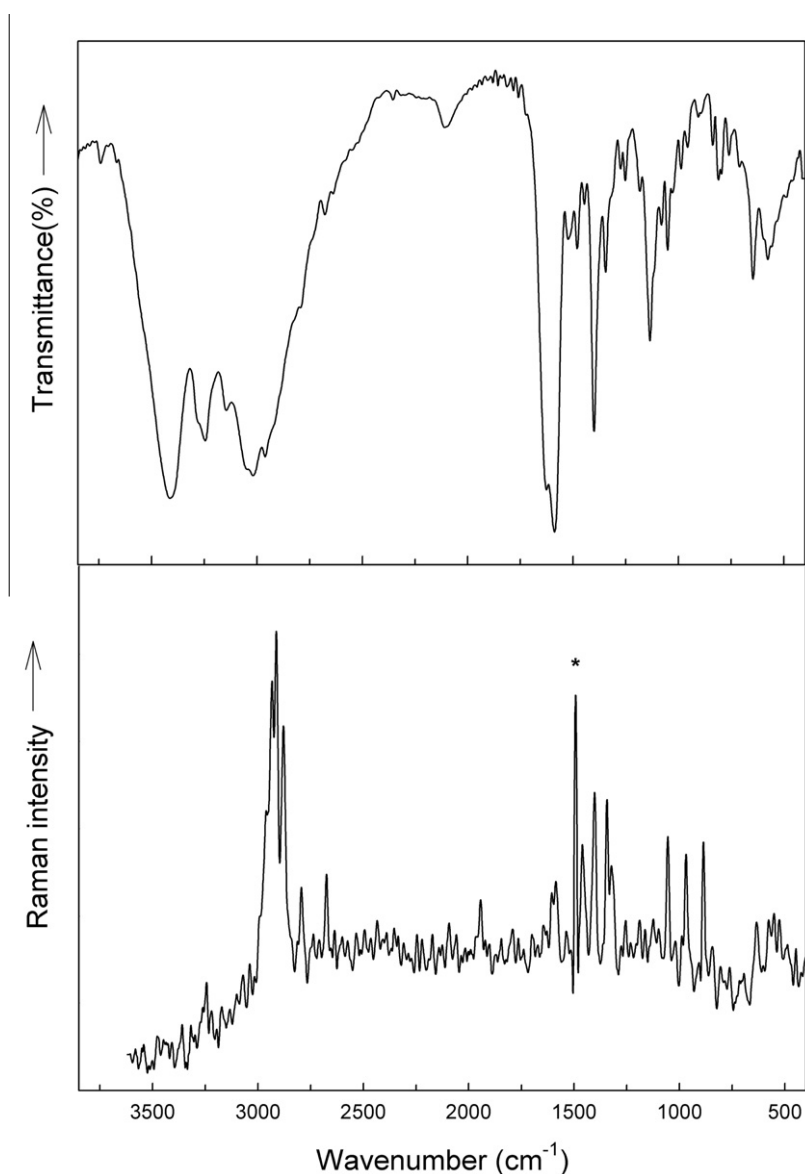


Fig. 1. Schematic structure of L-ornithine.

$\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  complex [19]. For comparative purposes, the positions of some of the most representative vibrations of this last complex are shown in Table 2.

The assignment proposed for  $[\text{Cu}(\text{L-orn})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  can be briefly analyzed and discussed as follows:

- The O–H stretching vibrations of the coordinated water molecules are seen as two very strong IR bands, but only one weak signal corresponding to the second of these bands can be observed in the Raman spectrum. The corresponding deformational band,  $\delta(\text{H}_2\text{O})$ , is probably overlapped by the strong IR band at about  $1600 \text{ cm}^{-1}$ .
- The N–H stretching vibrations of the terminal  $\text{NH}_3^+$  moiety are only seen as a relative weak band in both spectra, probably as a consequence of its partial overlap with the strong C–H stretching bands, in this region.
- The stretching vibrations of the  $\text{CH}_2$  groups generate a relatively broad IR doublet whereas in the corresponding Raman spectrum a very interesting and complex spectral pattern can be observed in this region. A similar spectral pattern was observed in the analogous  $[\text{Cu}(\text{L-lys})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  complex [19].
- The spectra shows a series of relatively weak or medium intensity bands in the region between  $2800$  and  $2600 \text{ cm}^{-1}$  which are characteristic for primary amine salts and are attributed to combination bands enhanced by Fermi resonance, involving the deformation vibrations [15]. Another characteristic feature of these spectra is the occasional appearance of an isolated band near  $2000 \text{ cm}^{-1}$ , usually assigned to a combination of the  $\delta_{\text{as}}(-\text{NH}_3^+)$  band and a  $\text{NH}_3^+$  torsional oscillation lying at about  $480 \text{ cm}^{-1}$  [15]. This band is found at  $2113 \text{ cm}^{-1}$  in the IR spectrum of the complex and as a somewhat stronger feature at  $2077 \text{ cm}^{-1}$ , in the IR spectrum of ornithine monohydrochloride [18]. In the Raman spectrum of the complex a doublet with components at  $1962$  and  $1945 \text{ cm}^{-1}$  is found in this region. Similar bands are also found in the case of  $[\text{Cu}(\text{L-lys})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  (cf. Table 2).
- The antisymmetric stretching vibration of the carboxylate group is seen as a very strong IR band at  $1589 \text{ cm}^{-1}$  with a weaker feature at its higher energy side ( $1626 \text{ cm}^{-1}$ ) and appears overlapped with the  $\delta_{\text{as}}(\text{NH}_3^+)$  motion. In the Raman spectrum a relatively complex band, with maximum at  $1609 \text{ cm}^{-1}$  is found in this region. The corresponding symmetric stretching vibration is found as a relatively strong and well defined IR band at  $1401 \text{ cm}^{-1}$  whereas its Raman counterpart lie at  $1403 \text{ cm}^{-1}$ . The energy difference between these two stretching vibrations (ca.  $190 \text{ cm}^{-1}$ ) supports clearly the fact that the carboxylate group of the amino acid acts as an unidentate ligand in this complex [20,21].
- As mentioned above, the  $\delta_{\text{as}}(\text{NH}_3^+)$  vibration appears overlapped with the  $\nu_{\text{as}}(\text{COO}^-)$  stretching but the  $\delta_{\text{s}}(\text{NH}_3^+)$  mode could be clearly identified as a separate band in both spectra ( $1480 \text{ cm}^{-1}$  (IR),  $1462 \text{ cm}^{-1}$  (Raman)). In the IR spectrum of ornithine monohydrochloride this band is found at  $1485 \text{ cm}^{-1}$  [18]. In the case of  $[\text{Cu}(\text{L-lys})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  the  $\delta_{\text{as}}(\text{NH}_3^+)$  vibration is clearly separated from the  $\nu_{\text{as}}(\text{COO}^-)$  stretching (cf. again Table 2).



**Fig. 2.** FTIR (above) and FT-Raman (below) spectra of  $[\text{Cu}(\text{l-orn})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  in the spectral range between 3750 and  $400\text{ cm}^{-1}$  (\* This Raman line ( $1492\text{ cm}^{-1}$ ) originates in an instrumental noise).

- Bending vibrations of the  $\text{CH}_2$  groups are found in the usual ranges [15,16] and the deformational vibrations of the carboxylate groups were assigned on the basis of the previous analyses of the related  $[\text{Cu}(\text{l-lys})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  complex [19].
- The position of the Cu-ligand vibrations is difficult to establish. It is known that in these types of complexes,  $\nu(\text{Cu-N})$  appears at somewhat higher energies than  $\nu(\text{Cu-O})$  [20,22] whereas Cu-Cl vibrations are expected between 400 and  $200\text{ cm}^{-1}$  [20].

#### Electronic spectrum of $[\text{Cu}(\text{l-orn})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$

The electronic absorption spectrum of an aqueous solution of the complex presents a strong and relatively broad band with maximum at 620 nm (molar absorption coefficient of  $47\text{ L mol}^{-1}\text{ cm}^{-1}$ ) and a weak shoulder at about 650 nm. At higher energies a very strong absorption located at 232 nm (molar absorption coefficient of ca.  $4830\text{ L mol}^{-1}\text{ cm}^{-1}$ ) is observed.

The broad band centered at 620 nm is characteristic for distorted octahedral Cu(II) complexes and involves the three expected

transitions from the  $d_{xy}$ ,  $d_z^2$ , and  $d_{xz}$ ,  $d_{yz}$  pair to the half filled  $d_{x^2-y^2}$  level [23].

We have analyzed the position of this band on the basis of the simple theoretical model of Prenesti et al. [24,25]. This model is based in an analysis of visible spectrophotometric data of more than 100 Cu(II) complexes formed by ligands with different coordination environments and allows the estimation of the  $\lambda_{\text{max}}$  values for equatorially-coordinated Cu(II) complexes in solution, using a simple summation which takes in account the number and chemical characteristics of the different donor ligands present in the coordination sphere [24]. The approach was later extended to include the effect of the axial coordination of the metal center [25]. Using this model, the calculation for the square planar  $\text{CuO}_2^{\text{carboxylate}}\text{N}_2^{\text{ammino}}$  environment gave a value of 623 nm, in excellent agreement with the experimental value, showing that in the present case the red shift usually expected after the incorporation of the two axially bonded (chloride) ligands [25] has a negligible effect on the energy of the observed d-d transition. In this context, it must be emphasized that the values calculated with this theoret-

**Table 1**Assignment of the infrared and Raman spectra of  $[\text{Cu}(\text{l-orn})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  (band positions in  $\text{cm}^{-1}$ ).

IR	Raman	Assignment
3418 vs, 3243 vs	3243 w	$\nu(\text{OH}) (\text{H}_2\text{O})$
3149 w	3163 vw	$\nu(\text{NH}) (\text{NH}_3^+)$
3020 vs	2995 w, 2960 m, 2933 s	$\nu_{\text{as}}(\text{CH}_2)$
	2913 vs	$\nu_{\text{as}}(\text{CH}_2)$
2966 m	2877 s	$\nu_{\text{s}}(\text{CH}_2)$
2802 sh, 2640 w, 2602 vw	2794 m, 2676 m	Combinations (cf. text)
2113 m	1962 w, 1945 m	Combinations (cf. text)
1626 w, 1589 vs	1609 m, 1586 m	$\nu_{\text{as}}(\text{COO}^-) + \delta_{\text{as}}(\text{NH}_3^+)$
1527 m, 1496 sh	1513 w, 1485 vw	$\delta(\text{CH}_2)$
1480 m, 1447 w	1462 s, 1448 sh	$\delta_{\text{s}}(\text{NH}_3^+)$
1401 vs	1403 s	$\nu_{\text{s}}(\text{COO}^-)$
1345 m, 1298 w, 1286 w	1345 s, 1326 s, 1312 sh	$\omega(\text{CH}_2)$
1275 m, 1252 m	1261 w, 1240 w	$\tau(\text{CH}_2)$
1184 w	1178 w	$\tau(\text{CH}_2)$
1186 sh, 1134 s	1160 w	$\rho(\text{NH}_3^+)$
1084 w, 1079 m	1055 s	$\nu(\text{C-N})$
1051 m		$\nu(\text{C-N})$
1024 w, 970 w, 837 w	990 w, 970 s, 958 sh	$\nu(\text{C-C})$
	920 w, 887 s	$\nu(\text{C-C})$
813 m	836 w	$\delta(\text{COO}^-)$
795 m, 762 m	790 w, 767 w	$\omega(\text{COO}^-)$
711 w, 648 m	634 m	$\omega(\text{COO}^-)$
621 vw, 577 w, 553 vw	576 m, 550 m, 525 m	$\nu(\text{COO}^-)$

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

**Table 2**Assignment of some characteristic infrared and Raman bands (in  $\text{cm}^{-1}$ ) of  $[\text{Cu}(\text{l-Lys})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  (from ref. [19]).

IR	Raman	Assignment
3141 w	3175 vw	$\nu(\text{NH}) (\text{NH}_3^+)$
2943 s	2867 s, 2842 sh	$\nu_{\text{s}}(\text{CH}_2)$
2018 m	2020 vw, 1946 w	Combinations (cf. text)
1660 vs	1680 vw, 1662 m	$\nu_{\text{as}}(\text{COO}^-)$
1583 vs	1624 w, 1586 s	$\delta_{\text{as}}(\text{NH}_3^+)$
1527 m, 1496 sh	1513 w, 1485 vw	$\delta(\text{CH}_2)$
1526 s	1523 w, 1483 m	$\delta_{\text{s}}(\text{NH}_3^+)$
1394 s	1409 m, 1394 m	$\nu_{\text{s}}(\text{COO}^-)$
1168 w, 1134 s	1167 m, 1135 w	$(\text{NH}_3^+)$
1110 w, 1079 m	1114 m, 1077 m	$\nu(\text{C-N})$
1047 m	1048 s, 1042 vs	$\nu(\text{C-N})$
806 w	802 w	$\delta(\text{COO}^-)$

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

ical model, include intrinsically the contribution of two water molecules along the z-axis of a distorted Cu(II) octahedron [25]. Therefore, and taking into account the relatively closeness of the aqua and chloride ligands in the spectrochemical series [23] the obtained result is clearly understandable.

The second spectral band, at 232 nm, is surely originated in a  $\text{Cl} \rightarrow \text{Cu}$  charge transfer transition.

To conclude, this investigation provides new insights into the vibrational-spectroscopic behavior of a mixed ligand Cu(II) complex of potential biological interest. Besides, the characteristics of its electronic absorption spectrum present a satisfactory agreement with a relatively simple but certainly useful theoretical model. All the obtained results are strictly comparable to those previously reported for the structurally analogous  $[\text{Cu}(\text{l-lys})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  complex, containing l-lysine instead of l-ornithine in the coordination sphere.

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