

## Spectroscopic and Magnetic Behaviour of the Copper (II) Complex of L-Tryptophan

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**SUMMARY.** A copper(II) complex of the amino acid L-tryptophan, of stoichiometry  $\text{Cu}(\text{Trp})_2$ , was obtained from aqueous solution. Its structural characteristics were deduced from the careful analysis of infrared, Raman and electronic absorption spectra, complemented with magnetic susceptibility measurements in the temperature range between 2 and 300 K. The metal center presents a distorted octahedral  $\text{CuN}_2\text{O}_4$  environment with a trans arrangement of the amino acids in the equatorial plane, involving the terminal amino and carboxylate groups. The coordination sphere is complemented with two longer apical Cu-O bonds involving "free" O-carboxylate atoms of neighboring complex moieties.

**RESUMEN.** "Comportamiento Espectroscópico y Magnético del Complejo de Cobre (II) con L-Triptofano". Un complejo de cobre (II) con el amino ácido L-triptofano, de estequiometría  $\text{Cu}(\text{Trp})_2$ , fue obtenido de solución acuosa. Sus características estructurales fueron deducidas en base a un pormenorizado análisis de sus espectros de infrarrojo, Raman y de absorción electrónica, complementado con medidas de susceptibilidad magnética en el intervalo de temperaturas entre 2 y 300 K. El centro metálico presenta un entorno  $\text{CuN}_2\text{O}_4$  octaédrico distorsionado con una disposición trans de los amino ácidos en el plano ecuatorial, involucrando los grupos amino y carboxilato terminales. La esfera de coordinación se complementa con dos enlaces Cu-O axiales más largos, involucrando átomos de oxígeno "libres" de grupos carboxilato de unidades complejas vecinas.

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### INTRODUCTION

As a continuation of our studies of the general physicochemical properties of copper complexes of amino acids with pharmacological activity<sup>1-5</sup>, we have now prepared and investigated the spectroscopic (vibrational and electronic) and magnetic behaviour of the corresponding complex of L-tryptophan, with  $\text{Cu}(\text{Trp})_2$  stoichiometry. As known, this complex presents an interesting anti-inflammatory, antiulcer and anti-convulsant activity<sup>6-9</sup>.

### MATERIAL AND METHODS

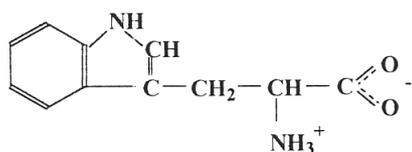
$\text{Cu}(\text{Trp})_2$  was prepared by reaction of L-tryptophan (Fig.1) and copper(II) chloride solutions in stoichiometric relation, in the following way:

1.82 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck) were dissolved in 40 mL of hot water. Another solution, containing 4.34 g of L-tryptophan (Sigma) in 50 mL of hot water was dropwise added to the copper solution, under continuous stirring. After mixing, the solution was stirred over a water bath during about half an hour. The complex precipitated in the form of a blue powder. It was filtered on a fritted glass funnel and washed several times with hot water until complete elimination of chlorides. Finally, the complex was recrystallized from dimethylsulfoxide/water and dried in vacuum over calcium chloride<sup>10</sup>. Analytical results: Found: Cu, 13.60; C, 56.10; N, 11.85; H, 4.85. Calculated for  $\text{Cu}(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2)_2$ : Cu, 13.52; C, 56.22; N, 11.92; H, 4.72%.

**KEY WORDS:** Bis(L-tryptophanate)Cu(II), Electronic spectrum, IR spectrum, Magnetic Susceptibility, Raman spectrum.

**PALABRAS CLAVE:** Bis(L-triptofanato)Cu(II), Espectro Electrónico, Espectro IR, Espectro Raman, Susceptibilidad Magnética.

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**Figure 1.** Schematic structure of L-tryptophan.

The complex is insoluble in water and in most of the usual organic solvents (methanol, ethanol, acetone and chloroform) and is slightly soluble, only in dimethylsulfoxide. Unfortunately, we could not obtain single crystals adequate for a X-ray structural analysis.

The infrared spectra of the free amino acid and the complex were recorded with a Perkin Elmer 580 B spectrophotometer in the spectral range between 4000 and 300  $\text{cm}^{-1}$ , using the KBr pellet technique. The Raman spectra were recorded with a Bruker IFS 66 FTIR instrument provided with a FRA 106 Raman accessory. The 1064 nm line of a Nd : YAG laser was used for excitation.

Electronic absorption spectra of the complex in DMSO were recorded in a Hewlett-Packard 8452 diode-array spectrophotometer, using 10-mm quartz cells.

The magnetic susceptibility measurements were performed with a Quantum Design SQUID MPMS XL-5 magnetometer in the temperature range between 2 and 300 K. The equipment was calibrated with metallic palladium and  $\text{Hg}[\text{Co}(\text{SCN})_4]$ . A magnetic field of 100 Oe was used.

## RESULTS AND DISCUSSION

### Vibrational spectra

As the crystal structure of the complex is so far unknown, the careful analysis of its infrared

and Raman spectra appear as especially interesting in order to attain a first insight into the structural peculiarities.

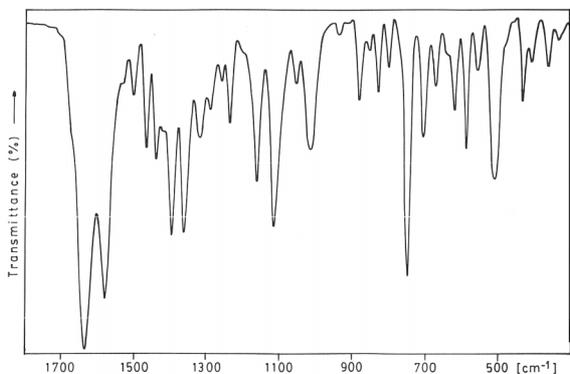
The most interesting IR-spectral range for the complex (1800-300  $\text{cm}^{-1}$ ) is shown in Figure 2 whereas the corresponding Raman spectrum, in the same range, is presented in Figure 3.

An approximate assignment for the most important and characteristic vibrational bands of pure L-tryptophan and its copper complex are presented in Table 1. This assignment is based on some general literature data<sup>11-14</sup> and by comparison with the results of our previous studies on similar Cu(II)/amino acid complexes<sup>3-5</sup> and is briefly commented, as follows:

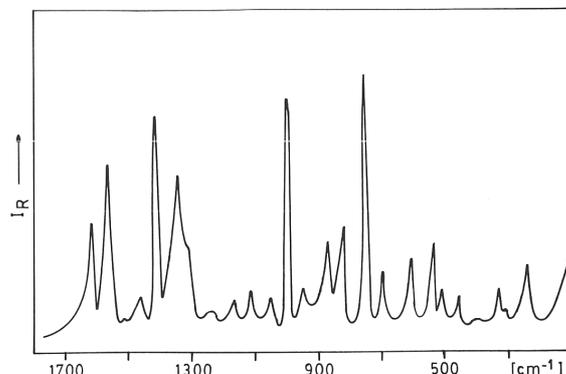
The presence of the characteristic  $\nu(\text{NH}_3^+)$  and  $\delta(\text{NH}_3^+)$  bands and the position of the carboxylate stretching vibrations in the free ligand, clearly confirms its existence in the *zwitterionic* form.

After complexation, the two  $\text{NH}_2$  stretching vibrations, together with some typical deformational motions of this group could be observed. The position of these bands clearly supports the involvement of this group in bonding. Also the aliphatic  $\nu(\text{C-N})$  stretching appears more affected than the corresponding vibration of the indol group.

The energy displacement observed for the carboxylate vibrations confirms also the participation of this group in copper coordination. However, this group shows an interesting and somewhat unexpected behaviour, which has also been observed in our previous studies<sup>3-5</sup>. In the "free" amino acid in its zwitterionic crystalline form two vibrations for the  $\text{COO}^-$  moiety are expected ( $\nu_s(\text{COO}^-)$  and  $\nu_{as}(\text{COO}^-)$  respectively). After coordination energy lowering of one of these bands is expected, due to the generation of the Cu-O bond and the increase of



**Figure 2.** Infrared spectrum of  $\text{Cu}(\text{Trp})_2$  between 1800 and 300  $\text{cm}^{-1}$ .



**Figure 3.** Raman spectrum of  $\text{Cu}(\text{Trp})_2$  between 1800 and 300  $\text{cm}^{-1}$ .

the other one, because a C–O double bond is partially reconstructed. As it can be seen from the data presented in Table 1, the IR band assigned to the  $\nu_s(\text{COO}^-)$  vibration in the “free” acid suffer a small shift to lower wavenumbers, in agreement with the participation of the C–O group in binding. Nevertheless, the other band is not reinforced as expected after complex formation. As in most of the previously investigated complexes <sup>3-5</sup> this band also suffers a small energy diminution, suggesting the involvement

of the “free” C=O unit in secondary bonds to the metal center.

In the Raman spectrum the  $\nu(\text{C–O})$  vibration is, apparently, coupled with one of the  $\text{CH}_2$  deformational modes.

A number of vibrational bands in the 700-500  $\text{cm}^{-1}$  range could not be assigned with certainty. They probably belong to complex coupled motions.

The assignment of the ligand to metal vibrations was also difficult, as the “free” amino acid

L-tryptophan		Cu(Trp) <sub>2</sub>		Assignment
IR	IR	Raman		
3403 vs	3390 vs	3385 w		$\nu(\text{N-H})$ indol
	3336 m			$\nu_{\text{as}}(\text{NH}_2)$
	3272 s	3275 w		$\nu_s(\text{NH}_2)$
3094 vs				$\nu_{\text{as}}(\text{NH}_3^+)$
	2908 s	3059 vs/2906 vs		$\nu(\text{CH})$
3027 vs				$\nu_s(\text{NH}_3^+) + \nu(\text{CH})$
1668 vs				$\delta(\text{NH}_3^+)$
1589 vs				$\nu_{\text{as}}(\text{COO}^-)$
	1626 vs	1615 m		$\delta(\text{NH}_2)$
	1578 vs	1570 m		$\nu(\text{C=O})$
1493 w				$\delta(\text{NH}_3^+)$
1459 s	1457 s	1458 w		$\delta(\text{CH}_2)$
	1429 m	1423 vs		$\delta(\text{CH}_2) + \nu\text{CO}$
1412 vs				$\nu_s(\text{COO}^-)$
	1385 vs			$\nu(\text{C–O})$
1353 vs	1357 vs	1350 s		$\nu(\text{C–N})$ indol
1317 m	1307 m	1310 sh		$\delta(\text{CH})$
1229 m	1225 m			$\tau(\text{CH}_2)$
1152 s				$\rho(\text{NH}_3^+)$
	1151 vs	1157 w		$\rho(\text{NH}_2)$
1097 s	1107 vs	1115 w		$\nu(\text{C–N})$ aliphatic
1076 m, 1055 w	1046 m	1046 w		Ring modes
1006m, 986m, 920s	1003 vs, 929 w	1007 vs, 946 w		Ring modes
857s, 845sh, 803 w	872 m, 822 m	876 m, 822 m		$\rho(\text{CH}_2)$
743 vs	737 vs	765 vs		$\delta(\text{COO}^-)$
681m, 624m, 585s	696s, 664m, 611s	699 w, 606 m		
554s, 526s, 502vs	581s, 549m, 502vs	546 m, 510 w		
	472 w	470 w		$\nu(\text{Cu–N})$
	457m, 425s, 397w	423m, 401 w		
349 s, 322 m	357 m, 330 w			
	314 sh	320 sh		$\nu(\text{Cu–O})$
		244 m		Cu-ligand bend

**Table 1.** Vibrational spectra of L-tryptophan (Trp) and of the  $\text{Cu}(\text{Trp})_2$  complex in the spectral range between 4000 and 300  $\text{cm}^{-1}$ ; vs: very strong; s: strong; m: medium; w; weak; vw: very weak; sh: shoulder.

presents an important number of bands in the lower frequency region. Notwithstanding, by comparison of its IR spectrum with that of the complex in the low frequency range using a FTIR instrument we could establish the presence of two new, relatively weak, bands in the last one. By comparison with literature data <sup>3,5,13,15</sup>, these bands could be assigned to these ligand-to-metal modes. Additionally, a medium intensity Raman peak at 244 cm<sup>-1</sup> was also assigned to a motion of the metal-to-ligand skeleton.

For complexes of this type *cis* or *trans* isomers could be generated and they can be differentiated by its infrared spectroscopic behaviour. For *cis*-isomers the appearance of two Cu-O and two Cu-N vibrational bands is expected, whereas for *trans* isomers only one band for each of these modes is predicted <sup>13,15</sup>. Therefore, the present results suggest that the obtained Cu(trp)<sub>2</sub> complex is the *trans* isomer.

### Electronic spectra

In order to attain a wider insight into the characteristics of the coordination sphere of the Cu(II) center, we have measured the electronic absorption spectrum of the complex in a DMSO solution. It presents a relatively broad band in the visible region, centered at about 612 nm, with a molar extinction coefficient  $\epsilon = 70 \text{ L mol}^{-1} \text{ cm}^{-1}$ . In octahedral or pseudo-octahedral environments this band is usually composed by a number of components <sup>16</sup>, that in the present case remain unresolved. These bands originated in transitions from the  $d_{xy}$ ,  $d_z^2$  and  $d_{xz}$ ,  $d_{yz}$  pair to the  $\sigma$  antibonding and half-filled  $d_{x^2-y^2}$  level and the relative order of these transitions will depend upon the extent of axial metal-ligand interaction and on the overall geometry around the metal center <sup>16</sup>. The  $\epsilon$ -value points to a centro-symmetric complex, supporting again the presence of a *trans* arrangement of the ligands <sup>16</sup>.

Finally, it is interesting to remark that the measured absorption maximum is in reasonable good agreement with the value of 622 nm, derived from the theoretical model recently developed by Prenesti *et al.* <sup>17</sup>.

### Magnetic susceptibility

The magnetic susceptibility was measured in the temperature range between 2 and 300 K. The analysis of data showed that the complex obeys a Curie-Weiss law of the type  $\chi^{-1}_M = -19 + 2.79 \text{ T}$  in the full temperature range. The effective magnetic moment obtained in the usual way, from the  $\chi^{-1}_M$  versus T plot, takes a value of 1.69 BM, which agrees with the value expect-

ed for a d<sup>9</sup> complex with S = 1/2 without couplings <sup>18</sup>, confirming the presence of a monomeric complex species.

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