

Vibrational Spectrum of the Copper(II) Complex of Anthranilic Acid

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SUMMARY. The infrared and Raman spectra of the $\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$ complex were recorded and briefly discussed in relation to its structural characteristics. The isostructural Zn(II) complex was also investigated for comparative purposes.

RESUMEN. "Espectro vibracional del complejo de cobre(II) con ácido antranílico". Se registraron los espectros de infrarojo y Raman del complejo $\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$ y se los discutió someramente en base a sus características estructurales. Con fines comparativos se investigó también el complejo isoestructural de Zn(II).

INTRODUCTION

The role of copper in relation to inflammatory diseases is not straightforward and has often given rise to paradoxical interpretations^{1,2}. However, it has long been established that inactive substances can become potent antiinflammatory agents when administered as their copper complexes and, in particular, that copper complexes of non-steroidal antiinflammatory agents are much more effective than their parent drugs¹⁻⁴.

We have recently initiated systematic studies of copper complexes with non-steroidal antiinflammatory drugs derived from N-phenylanthranilic acid and have investigated the structural and spectroscopic behavior of the dimeric Cu(II) complexes of N-2,3-dimethylphenylanthranilic acid (mefenamic acid)⁵ and N-3-trifluorophenylanthranilic acid (flufenamic acid)⁶.

During the study of these complexes, and in order to attain a better understanding of their vibrational-spectroscopic behavior, we have also performed an investigation of the IR and Raman spectra of the mononuclear Cu(II) complex of anthranilic acid (o-amino-benzoic acid). The results of this investigation, complemented with some spectroscopic data for a similar Zn(II)

complex, constitute the main subject of this paper.

Besides, it should be emphasized that it has been recently demonstrated that anthranilic acid presents an important OH radical scavenging potential, which is a direct function of the fraction of Cu(II) bound to it².

EXPERIMENTAL

Micro-crystalline samples of the bis(anthranilato)Cu(II) complex were obtained by slow addition of a 1 M aqueous solution of copper(II) nitrate to a stoichiometric quantity of a 0.2 M aqueous solution of the sodium salt of the acid⁷. The complex, in form of a blue powder, immediately precipitated and was separated by filtration and washed three times with small portions of water and finally with diethyl ether. It was stored in a vacuum desiccator over H_2SO_4 . The similar Zn(II) complex was obtained by an analogous procedure, starting with a zinc nitrate solution. The purity of both complexes was checked by chemical analysis and X-ray diffraction.

The spectra were obtained with a Bruker FTIR IFS 66 instrument, provided with a FRA 106 Raman accessory. IR spectra were recorded

KEY WORDS: Cu(II), Anthranilic Acid, Antinflammatory Drugs.

PALABRAS CLAVE: Cu(II), Acido Antranílico, Drogas Antiinflamatorias.

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using the KBr pellet technique. For the Raman measurements, excitation of the samples was accomplished with the 1064 nm radiation of a Nd:YAG solid state laser.

RESULTS AND DISCUSSION

Crystal structure of the complex

$\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$ belongs to the monoclinic space group $P2_1/c$ with $Z = 2$ ⁸. Coordination around the metal center is a distorted octahedron. The four equatorial positions are occupied by two amino nitrogens and two carboxylate oxygens with both the nitrogens and oxygens in *trans* positions. The coordination is completed

in the axial positions by two carbonyl oxygens, each of which belongs to a different anthranilate to ligand. The result of this mode of coordination is that each Cu(II) ion interacts with four other ions via carboxylate bridges, generating a two-dimensional polymeric sheet structure⁸.

Infrared and Raman spectra

The FTIR spectrum of the complex, between 4000 and 400 cm^{-1} is shown in Figure 1, whereas the most characteristic and useful part of the Raman spectrum is reproduced in Figure 2. Both spectra are rather complex and it is impossible to propose a complete assignment for them without additional experimental data.

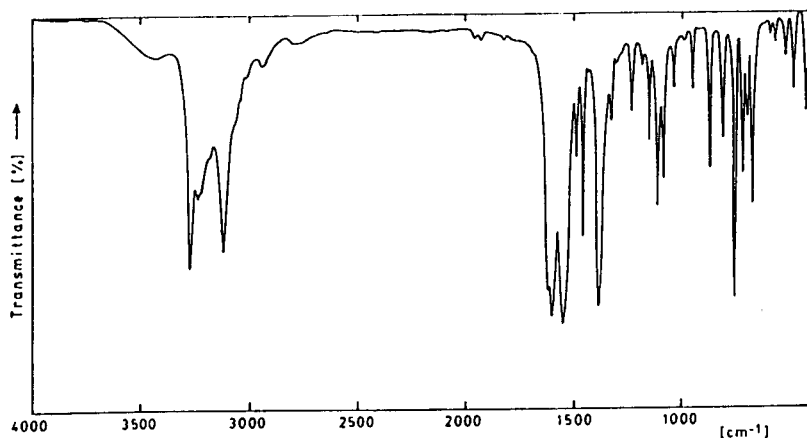


Figure 1. FTIR spectrum of $\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$

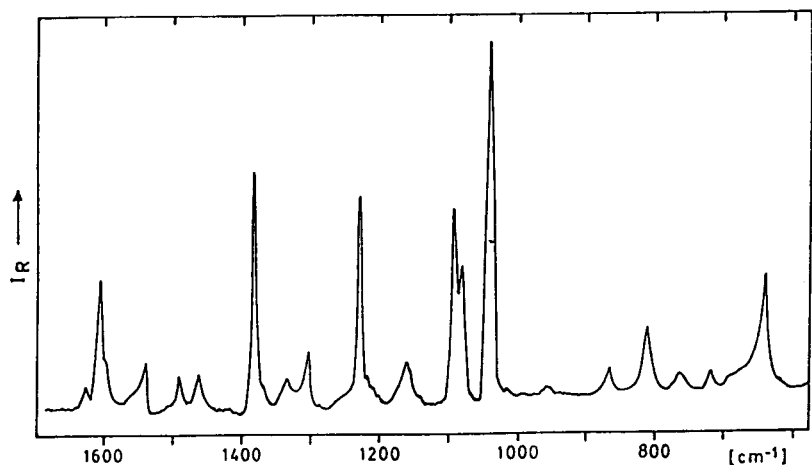


Figure 2. FT-Raman spectrum of $\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$ between 1700 and 600 cm^{-1}

Our assignment, based mainly on general spectral data reported in standard references⁹⁻¹¹, is presented in Table 1 and can be briefly commented as follows:

In the higher frequency region the stretching bands of the $-\text{NH}_2$ groups clearly dominates both spectra. The ν_s vibration originates the strongest Raman line in this region. In the free acid the IR bands related to this vibrations are

found at 3502 and 3387 cm^{-1} ¹¹ and as expected, after complexation, both vibrations suffer an important shift to lower frequencies. Moreover, after complexation a third, weaker peak, appears intercalated between these two $\nu(\text{NH}_2)$ bands. The appearance of this new peak was also observed in some other metallic complexes of anthranilic acid and related ligands⁷.

Other characteristic vibrations related to the

Infrared	Raman	Assignment
3275 vs	3274 vw	$\nu_{as}(\text{NH}_2)$
3240 w, 3220 sh	3239 vw	
3188 sh	3179 vw	
3122 vs	3122 vs	$\nu_s(\text{NH}_2)$
3042 vw, 304 vw	3100 w	$\nu(\text{C-H})$
2937w, 2791vw, 2320vw		
1961vw, 1927w, 1826vw		combinations of δ_{wagg}
1626 sh, 1606 vs	1625 w, 1602 m	$\delta_{sciss}(\text{NH}_2) + \nu(\text{CC})_{ring}$
1548 vs	1545 w	$\nu_{as}(\text{COO}^-)$
1493 m	1491 w	$\nu(\text{CC})_{ring}$
1460 s	1461 w	$\nu(\text{CC})_{ring} + \delta(\text{CH})$
1385 vs	1384 s	$\nu_s(\text{COO}^-)$
1327	1330 w	$\nu(\text{C-CO}_2)$
	1301 w	
1232 m	1236 s	$\nu(\text{C-CO}_2)$
1170 w		$\nu(\text{CC})_{ring}$
1153 m	1164 w	$\nu(\text{CC})_{ring} + \delta(\text{CH})$
1115 s, 1081 s	1094 s, 1078 m	$\nu(\text{C-N})$
1038 m	1040 vs	$\nu(\text{CC})_{ring}$
965 vw, 953 m		$\delta_{wagg}(\text{CH})$
872 s	870 w	$\delta_{wagg}(\text{CH})$
810 s	817 m	
760 vs	763 vw	$\delta_{wagg}(\text{CH})$
715 s	720 vw	
695 m	695 sh	$\delta_{wagg}(\text{NH})$
670 s	670 m	$\rho(\text{COO}^-)$
590 w, 568 w		
519 m		
482 m	485 vw	$\nu(\text{Cu-N})$
420 s	422 sh	
	410 m	
	326 vw	$\nu(\text{Cu-O})$
	266 w	
	157 vs, 127 s, 85 vs	lattice modes

Table 1. Proposed assignment of the Infrared and Raman spectra of $\text{Cu}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$ (band positions in cm^{-1}). vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

amino group could also be clearly assigned in different spectral ranges. The scissoring deformation mode appears partially overlapped with one of the characteristic C-C ring motions, as often found in similar aromatic compounds.

The behavior of the carboxylate group is in agreement with the structural information. In the free ligand the C=O stretching vibration is found at 1667 cm^{-1} , whereas the C-OH stretching lies at 1292 cm^{-1} ¹¹. After deprotonation and complexation the carboxylate anion shows its anti-symmetric stretching as a very strong IR band at 1548 cm^{-1} with a weak Raman counterpart at 1545 cm^{-1} . The corresponding symmetric mode

lies at 1385 cm^{-1} in the IR spectrum and also appears as a strong Raman line at practically the same energy. Benzoate salts present these bands in the $1561\text{-}1552$ and $1427\text{-}1380 \text{ cm}^{-1}$ regions¹². The energy difference between the two $\nu(\text{COO}^-)$ stretchings in the complex is of 163 cm^{-1} and both vibrations are close to the free ion values, a behavior which is characteristic for carboxylate groups bridging two metal centers¹³.

In the case of the ring vibrations a number of C-C and C-H vibrations could be confidently assigned, as they lie clearly in the regions expected for an *ortho* substituted benzene ring^{9,10}. Interestingly, also a number of combination

Infrared	Raman	Assignment
3300 vs	3297 w	$\nu_{as}(\text{NH}_2)$
3132 vs	3058 vs	$\nu_s(\text{NH}_2)$
1616 s, 1594 vs	1617 w, 1602 m	$\delta_{sciss}(\text{NH}_2) + \nu(\text{CC})\text{ring}$
1594 vs		$\nu_{as}(\text{COO}^-)$
1408 vs	1403 s	$\nu_s(\text{COO}^-)$
1051 s	1044 vs	$\nu(\text{C-N})$
870 s	865 w	$\delta_{wagg}(\text{CH})$
754 vs	752 vw	$\delta_{wagg}(\text{CH})$
463 vw	463 w	$\nu(\text{Zn-N})$
	347 w	$\nu(\text{Zn-O})$

Table 2. Assignment of the most characteristic vibrational bands of $\text{Zn}(\text{NH}_2\text{C}_6\text{H}_4\text{COO})_2$ (band positions in cm^{-1}). vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

bands of the C-H-wagging motions¹⁰ could be identified between 1800 and 2000 cm^{-1} (cf. Table 1).

For the assignment of the metal-to-ligand vibrations we compared the present spectra with those of recently investigated Cu(II) complexes of amino acids presenting also O and N donors in *trans* position^{14,15}. In these cases the $\nu(\text{Cu-N})$ stretching usually lies around 450 cm^{-1} , whereas $\nu(\text{Cu-O})$ vibrations were found around 300 cm^{-1} . Therefore, we have assigned the medium intensity IR band located at 482 cm^{-1} , and its very weak Raman counterpart at 485 cm^{-1} to the $\nu(\text{Cu-N})$ vibration. In this region the free ligand shows neither Raman nor IR bands¹¹. Another very weak Raman signal, located at 326 cm^{-1} , has been tentatively assigned to the $\nu(\text{Cu-O})$ mode.

Comparisons with the Zn(II) complex

The structural study of the similar Zn(II) complex revealed that it is isostructural with the Cu(II) compound¹⁶. An important difference is that the coordination sphere around the Zn(II) ion is more regular as in the case of the copper complex, due to the expected Jahn-Teller distortion in this last case. The Zn-O distances are most shorter but apical Zn-O and equatorial Zn-O distances present similar values¹⁶, whereas Cu-O apical distances are appreciably longer than the equatorial ones⁸. In order to verify if these structural differences have any effect on the spectroscopic behavior, we have also measured the IR and Raman spectra of the zinc complex. The positions of the most important and characteristic bands are shown in Table 2. Only those vibrations directly related to the coordination sphere shall be briefly discussed as follows:

The $\nu(\text{NH}_2)$ stretching modes lie somewhat higher than in the Cu(II) complex, suggesting a somewhat weaker Zn-N interaction in agreement with the fact that the Zn-N bonds are slightly longer than the respective Cu-N bonds^{8,16}.

The $\nu_{as}(\text{COO}^-)$ vibration is identical to that of the copper complex, whereas the respective $\nu_s(\text{COO}^-)$ mode lies slightly higher. The difference between both vibrations is of 141 cm^{-1} . This behavior shows clearly that the small differences in symmetry of the coordination spheres, only has a negligible effect on the characteristics of the carboxylate vibrations.

The 482 cm^{-1} IR band is absent in this spectrum, supporting its assignment as a $\nu(\text{Cu-N})$ mode.

Bands assigned to Zn-to-ligand bonds are only proposed tentatively due to its very low intensity in both spectra.

To conclude, it should be remarked that, as expected, the general spectral pattern of the Zn(II) complex closely resembles that of the Cu(II) species and most of the typical bands related with ring modes are found in practically identical positions in the spectra of both compounds.

Acknowledgments. This work was supported by the *Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina* and the *Agencia Nacional de Promoción Científica y Tecnológica* (PICT Nr.119). It is also a part of a joint research project of the Inorganic Chemistry groups in Montevideo and La Plata, supported by both Universities. The authors are also indebted to LANAIS-EFO (La Plata) for the spectroscopic measurements.

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