

## Complexes of Ni(II) and Cu(II) with ofloxacin Crystal structure of a new Cu(II) ofloxacin complex

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### Abstract

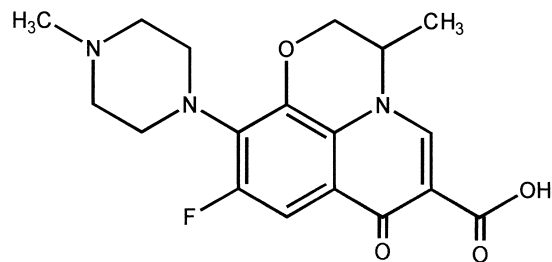
Several coordination compounds formed between Ni(II) or Cu(II) with ofloxacin have been synthesised and characterised. According to elemental chemical analysis and FT-IR spectroscopy data, direct reaction of Ni(II) and Cu(II) salts with ofloxacin leads to formation of precipitates for which mass spectrometry demonstrates their polymeric nature. However, crystalline  $[\text{Cu}(\text{oflo})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  is formed if the reaction is carried out in the presence of ammonia. This complex crystallises in the triclinic system, space group *P*-1 with  $a=9.2887(12)$ ,  $b=11.2376(14)$ ,  $c=17.874(2)$  Å,  $\alpha=92.12(3)$ ,  $\beta=95.39(3)$ ,  $\gamma=91.71(3)^\circ$  and  $Z=2$ . The local geometry around the Cu(II) ion is a slightly distorted square base pyramid. Electronic spectra, magnetic susceptibility measurements and EPR spectra of the synthesised complexes indicate a tetragonal environment. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Ofloxacin; Quinolones; Nickel complexes; Copper complexes

### 1. Introduction

Ofloxacin ((±)-9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido[1,2,3-de]-1,4-benzoxazine-6-carboxylic acid), is a nalidixic acid analog with broad spectrum antibacterial activity (Scheme 1). It belongs to the fluorquinolones group, which act as specific inhibitors of the bacterial DNA-gyrase, the enzyme responsible for converting double-stranded DNA into a negative superhelical form [1].

Studies of interaction between several quinolones with



Scheme 1.

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metal cations have been reported in the literature, specially those dealing with cinoxacin [2–6], although some studies on coordination compounds between ofloxacin (hereafter oflo) or ciprofloxacin with metal cations commonly found in several drugs used as antacids have been also reported [7]. These studies have been mainly directed towards identifying the groups directly attached to the metal site, and establishing the structure of the coordination compounds thus formed. In the present work, we report on the interaction between several Cu(II) and Ni(II) salts with oflo, analysing the effect of the counteranion in the starting metal salt on the nature of the compound finally formed, as well as the role of such anions on the groups relevant in the coordination to such a cation, determining by X-ray diffraction (XRD) procedures the molecular structure of one of the complexes isolated.

### 2. Experimental

#### 2.1. Materials and methods

Ofloxacin was provided by Sigma and all reagents used were of analytical grade.

Chemical analyses for carbon, hydrogen, and nitrogen

were performed on a 2400 elemental analyzer from Perkin-Elmer. Nickel and copper were determined on a ICP spectrometer (Perkin-Elmer model 2380 Plasma 2).

IR spectra were recorded using KBr mulls and a Perkin-Elmer FT-IR instrument. Electronic spectra were recorded on a Shimadzu UV-240 double beam with a diffuse reflectance accessory and a Hewlett-Packard 8452A diode spectrophotometers.

The room-temperature magnetic moment was measured by the Faraday method on a AZTEC DSM8 pendulum-type susceptometer and electron paramagnetic resonance spectra were recorded at X-band frequencies with a Bruker ER 200D.

The water content in the complexes was determined by thermal analysis, using a Perkin-Elmer TGA-7 thermobalance and a DTA-7 differential thermal analysis apparatus, both operating at a heating rate of 5°C/min and under oxygen as the reaction atmosphere.

Molecular masses were measured by Servicio de Masas (Universidad Autónoma de Madrid, Spain) by the FAB method with samples held on a nitrobenzyl alcohol (NBA) matrix and L-SIMS ionization mode, in a VG Autospec apparatus; the source was maintained at 30°C and 35 keV, and Cs<sup>+</sup> ion were used.

## 2.2. Syntheses of the complexes

The complexes have been prepared by direct reaction

Table 1

Crystal data and structure refinement for [Cu(oflo)<sub>2</sub>](H<sub>2</sub>O)·2H<sub>2</sub>O

Empirical formula	C <sub>36</sub> H <sub>44</sub> CuF <sub>2</sub> N <sub>6</sub> O <sub>11</sub>
Formula weight	838.31
Temperature	293(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1 (No. 2)
Unit cell dimensions	
<i>a</i> (Å)	9.2887(12)
<i>b</i> (Å)	11.2376(14)
<i>c</i> (Å)	17.874(2)
$\alpha$ (°)	92.12(3)
$\beta$ (°)	95.39(3)
$\gamma$ (°)	91.71(3)
Volume (Å <sup>3</sup> )	1855.1(4)
<i>Z</i>	2
Calculated density (mg/m <sup>3</sup> )	1.501
Absorption coefficient (mm <sup>-1</sup> )	0.668
<i>F</i> (000)	874
Crystal size (mm)	0.37×0.20×0.06
$\theta$ range for data collection (°)	1.81–28.06
Limiting indexes	– 8 = <i>h</i> = 12 – 14 = <i>k</i> = 11 – 23 = <i>l</i> = 19
Reflections collected/unique	11012/7673 [ <i>R</i> <sub>int</sub> = 0.0547]
Completeness to $\theta = 28.06$ (%)	85.1
Max. and min. transmission	1.000 and 0.644
Data/restraints/parameters	7673/0/543
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.878
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0703, <i>wR</i> <sub>2</sub> = 0.1433
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1617, <i>wR</i> <sub>2</sub> = 0.1698
Largest diff. peak and hole (e/Å <sup>3</sup> )	0.571 and –0.456

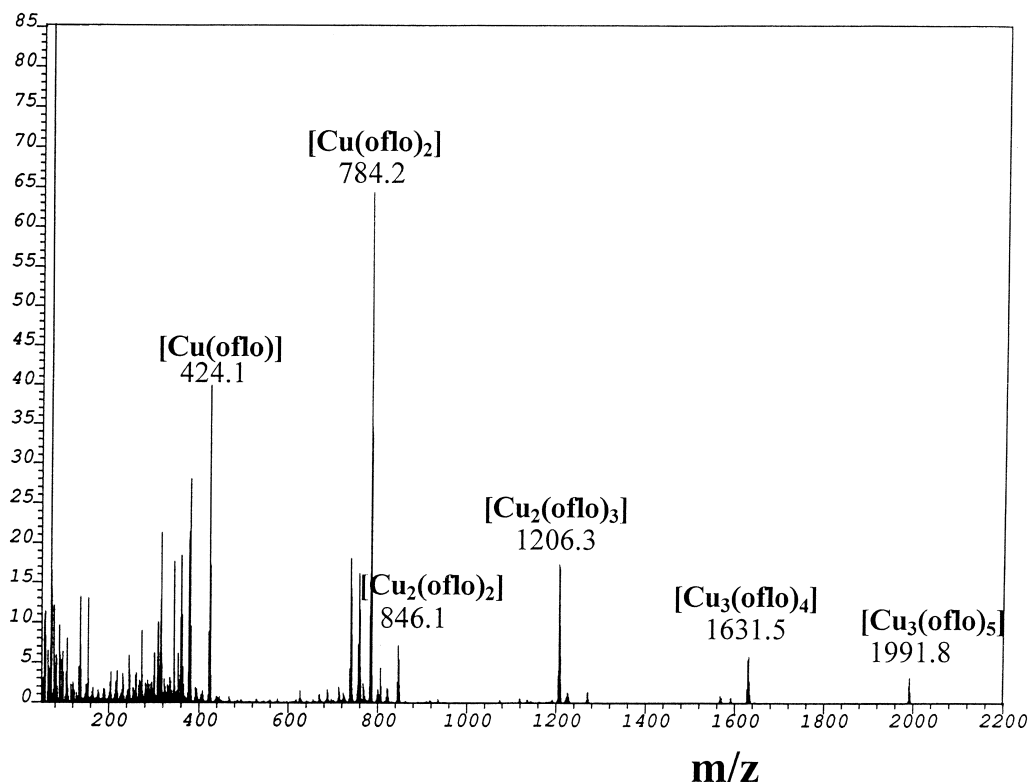


Fig. 1. FAB<sup>+</sup> MS spectra for the compound Cu(oflo)Cl·2.5H<sub>2</sub>O.

between oflo with the corresponding metal cations in the form of water-soluble salts, such as chlorides, sulphates or nitrates. Although in preliminary studies 0.1 M NaOH was added to the solution in order to improve solubility of oflo, it was observed that addition of the metal cation gave rise to the same effect, the nature of the complexes formed being independent on the presence of NaOH. A typical procedure was as follows: 0.41 mmol of the metal salt dissolved in 5 ml H<sub>2</sub>O were added to a magnetically stirred solution containing 0.82 mmol oflo suspended in 25 ml H<sub>2</sub>O. As the amount of cation added was increased, oflo dissolved, the solution attaining an emerald-green colour in the case of Ni(II); the concentration of the final solution (by elimination of the solvent or by drying in a desiccator with concentrated sulphuric acid) gave rise to a bright green precipitate with a sponge-like aspect, which was filtered and washed with distilled water. For the copper salts, the solution becomes deep blue and shortly after completing the addition of the salt a greenish-blue precipitates is formed, which is filtered and washed also with distilled water. The solids formed have very low solubility in water, probably because of their polymeric nature (see below). Yields were greater than 90% in both cases. Experimental data fit well with the calculated formula if the presence of crystallization water molecules is assumed, as checked by thermal analysis. Ni(oflo)(SO<sub>4</sub>)<sub>0.5</sub>·2.5H<sub>2</sub>O. Calc.: C, 42.2; H, 4.7; N, 8.2; Ni, 11.5; H<sub>2</sub>O loss, 8.9. Found: C, 42.6; H, 4.9; N, 8.2; Ni, 10.9; H<sub>2</sub>O loss 9.4. Ni(oflo)Cl·2.5H<sub>2</sub>O. Calc.: C, 43.3; H, 4.8; N, 8.4; Ni, 11.8; H<sub>2</sub>O loss, 9.0. Found: C, 43.7; H, 4.9; N, 8.1; Ni, 11.4; H<sub>2</sub>O loss, 9.1. Ni(oflo)(NO<sub>3</sub>)·2.5H<sub>2</sub>O. Calc.: C, 41.1; H, 4.6; N, 10.7; Ni, 11.2; H<sub>2</sub>O loss, 8.6. Found: C, 41.2; H, 4.8; N, 10.9; Ni, 10.9; H<sub>2</sub>O loss, 8.3. Cu(oflo)<sub>2</sub>(SO<sub>4</sub>)<sub>0.5</sub>·2.5H<sub>2</sub>O. Calc.: C, 41.8; H, 4.7; N, 8.1; Cu, 12.3; H<sub>2</sub>O loss, 8.7. Found: C, 42.0; H, 4.9; N, 8.1; Cu, 12.2; H<sub>2</sub>O loss, 8.8. Cu(oflo)Cl·2.5H<sub>2</sub>O. Calc.: C, 42.9; H, 4.8; N, 8.3; Cu, 12.6; H<sub>2</sub>O loss, 8.9. Found: C, 42.7; H, 5.0; N, 8.4; Cu, 12.2; H<sub>2</sub>O loss, 9.9. Cu(oflo)(NO<sub>3</sub>)·2.5H<sub>2</sub>O. Calc.: N, 40.7; H, 4.6; N, 10.6; Cu, 12.0; H<sub>2</sub>O loss, 8.5. Found: C, 41.1; H, 4.7; N, 10.8; Cu, 12.2; H<sub>2</sub>O loss, 8.5.

Under the experimental conditions used, it was not possible to isolate the compounds in a crystalline form, but single crystals were isolated if the synthesis is carried out in the presence of ammonia as follows: 0.35 mmol of the metal salt are added to 0.7 mmol oflo previously dissolved in 10 ml of 1 M NH<sub>3</sub>. A bright green (in the case of nickel) or deep blue (in the case of copper) solution is formed, although in the case of the copper solution, it turns into emerald-green after a few hours. Crystals, which are separated by filtration, are formed after 2 or 3 days.

Ni(oflo)<sub>2</sub>·3H<sub>2</sub>O. Calc.: C, 51.8; H, 5.3; N, 10.1; Ni, 7.0; H<sub>2</sub>O loss, 6.5. Found: C, 51.6; H, 5.4; N, 10.2; Ni, 7.4; H<sub>2</sub>O loss, 6.8. [Cu(oflo)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]·2H<sub>2</sub>O. Calc.: C, 51.3; H, 5.3; N, 10.0; Cu, 7.6; H<sub>2</sub>O loss, 6.4. Found: C, 51.4; H, 5.5; N, 10.2; Cu, 7.9; H<sub>2</sub>O loss, 6.7. The Cu-complex

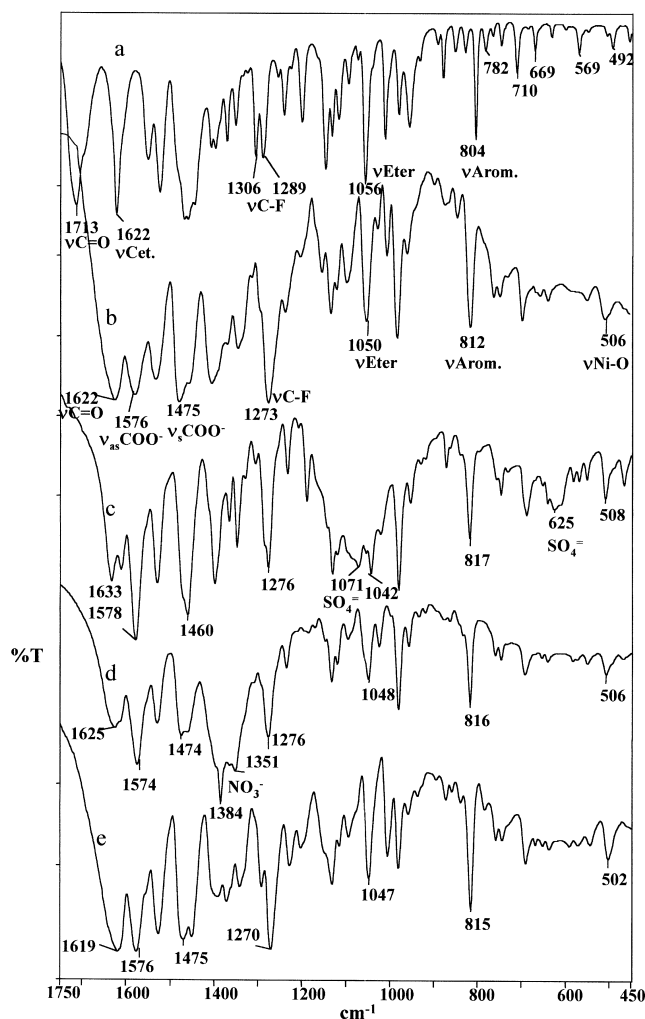


Fig. 2. FT-IR spectra for the compounds: (a) ofloxacin, (b) Ni(oflo)Cl·2.5H<sub>2</sub>O, (c) Ni(oflo)(SO<sub>4</sub>)<sub>0.5</sub>·2.5H<sub>2</sub>O, (d) Ni(oflo)(NO<sub>3</sub>)·2.5H<sub>2</sub>O and (e) Ni(oflo)<sub>2</sub>·3H<sub>2</sub>O.

Table 2

Selected bond lengths (Å) and angles (°) for [Cu(oflo)<sub>2</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O<sup>a</sup>

Cu(1)–O(11)	1.911(3)
Cu(1)–O(31)	1.922(3)
Cu(1)–O(13)	1.943(3)
Cu(1)–O(33)	1.956(3)
Cu(1)–O(1)	2.198(7)
O(2)–O(11)#1	2.870(7)
O(11)–Cu(1)–O(31)	170.05(17)
O(11)–Cu(1)–O(13)	92.97(14)
O(31)–Cu(1)–O(13)	86.29(14)
O(11)–Cu(1)–O(33)	86.16(14)
O(31)–Cu(1)–O(33)	92.08(14)
O(13)–Cu(1)–O(33)	165.61(16)
O(11)–Cu(1)–O(1)	93.9(2)
O(31)–Cu(1)–O(1)	96.0(2)
O(13)–Cu(1)–O(1)	100.6(2)
O(33)–Cu(1)–O(1)	93.8(2)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 x + 1, y, z.

crystals prepared could be analysed by XRD in order to determine their crystalline structure; unfortunately, the Ni complex crystals did not give rise to adequate diffractions.

### 2.3. X-ray structure determination of $[\text{Cu}(\text{oflo})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

A light green block crystal of  $[\text{Cu}(\text{oflo})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  was mounted on a glass fiber and used for data collection. Crystal data were collected at 291 K using a Bruker Smart CCD 1000 diffractometer. Graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ) was used throughout. The data were processed with SAINT [8] and corrected for absorption using SADABS (transmission factors: 1.000–0.644) [9]. The structure was solved by direct methods using the program SHELXS-86 [10] and refined by full-matrix least-squares techniques against  $F^2$  using SHELXL-97 [11]. Positional and anisotropic atomic displacement parameters were refined for all nonhydrogen atoms. Hydrogen atoms were located from difference syntheses and refined isotropically. The H atoms of two water molecules, O(2) and O(3) in the next tables, were not located. Atomic scattering factors were from the International Tables for X-ray Crystallography [12]. Molecular graphics were from PLATON [13]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

## 3. Results and discussion

### 3.1. Mass spectrometry

The results obtained support the assumption above about the polymeric nature of the compounds isolated. As shown in Fig. 1 for the Cu complex prepared from the chloride, peaks due to  $m/z$  values corresponding to different stoichiometries (depicted in Fig. 1) are recorded, in addition to the most intense signal at  $m/z=784.2$ , corresponding to the molecular ion,  $[\text{Cu}(\text{oflo})_2]^+$ , and that at  $m/z=424.1$ , corresponding to  $[\text{Cu}(\text{oflo})]^+$ . Similar results were also obtained for the Ni complexes, although in this case they are associated with the NBA matrix. It can be tentatively concluded that the original polymer is broken into different fragments, with different sizes, in the ionization chamber. Both the water molecules and the counteranions seem to be absent in the detected ionic fragments, so we may conclude they are only weakly bonded to the main fragments.

### 3.2. IR spectra

Although the counteranions are not detected by MS, their presence in the solids isolated is definitively concluded from the FT-IR spectra. So, bands are detected at  $1071$  and  $625 \text{ cm}^{-1}$  (sulphate) or  $1351 \text{ cm}^{-1}$  (nitrate) [14]

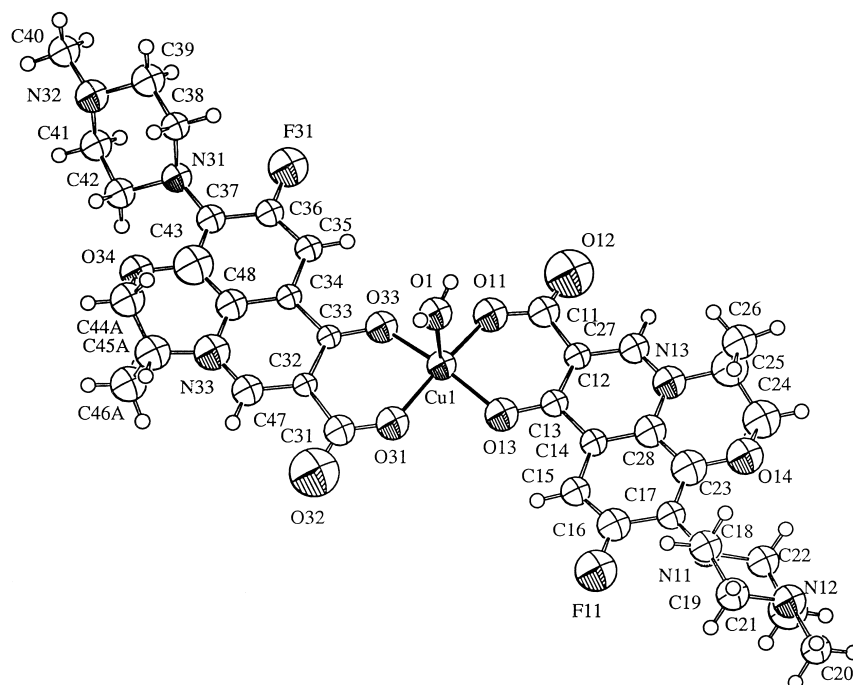


Fig. 3. ORTEP diagram for  $[\text{Cu}(\text{oflo})_2 \cdot \text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$  with the atom-labelling scheme.

in Fig. 2. The band at  $1713\text{ cm}^{-1}$  due to the carboxylic group is not detected in the spectra of any of the complexes, indicating that this moiety participates in the bonding to the metal ion [15]. However, the technique does not permit a definitive conclusion about the participation of the ketonic group in the bonding to the metal; the corresponding band is recorded at  $1622\text{ cm}^{-1}$  in the spectrum of oflo, and a band close to this position in the spectra of the complexes could be due to the ketonic group or to the carboxylate group bonded to the metal ion. If this band is due to the ketonic group, the antisymmetric and symmetric modes of the carboxylate group would account for the bands recorded at  $1575$  and  $1570\text{ cm}^{-1}$ , respectively. However, if the ketonic group participates in the bonding to the metal we would expect a shift of its stretching band towards lower wavenumbers, thus corresponding to the band recorded at  $1575\text{ cm}^{-1}$ , and the bands at  $1620$  and  $1470\text{ cm}^{-1}$  would correspond to the carboxylate group. We should conclude that FT-IR spectroscopy, by itself, does not permit a definitive answer to the way the ligand is bonded to the metal cation. Finally, the band at  $508\text{ cm}^{-1}$  could be ascribed to the Ni–O stretching mode [2,4]. The IR spectra of the Cu(II) complexes are similar to that Ni(II) complexes.

### 3.3. Crystal structure of $[\text{Cu}(\text{oflo})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

An ORTEP diagram of the complex  $[\text{Cu}(\text{oflo})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  including the atomic numbering scheme is shown in Fig. 3 and selected bond distances and angles are presented in Table 2. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 3.

The crystalline structure data definitively demonstrates the participation of the ketonic group of the oflo molecule in the bonding to the metal cation, the Cu(II) cation becoming five coordinated in a square base pyramidal structure. The copper atom is located  $0.205\text{ \AA}$  above the average plane defined by oxygens O11, O31, O13 and O33, which deviate from such average plane  $0.039\text{ \AA}$  above (O11 and O31) and  $0.039\text{ \AA}$  below (O13 and O33). The apical position would be occupied by a water molecule and the four corners of the base would be occupied by four oxygen atoms, two from the carboxylate groups and the two remaining from the ketonic groups (from two oflo molecules). The metal atom placed in a crystallographic inversion centre relates the two bidentate oflo ligands that bind through one oxygen of the carboxylate group and the exocyclic carbonyl oxygen. The Cu–O distances are similar to those reported previously for the corresponding complex with cinoxacin [5]. The geometry is not totally regular, although distortions are not too severe. The Cu–O (carboxylate) distances are slightly lower than the Cu–O (ketonic) distances. The O–Cu–O angles of a given oflo molecule are larger than the O–Cu–O angles with oxygen atoms from different oflo molecules, although this effect could also arise from the intrinsic structure of the oflo

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	$U_{\text{eq}}^a$
Cu(1)	314(1)	2341(1)	3033(1)	40(1)
F(11)	3367(4)	2153(2)	6647(2)	63(1)
F(31)	-3017(4)	2497(2)	-510(2)	60(1)
O(1)	2361(7)	2472(5)	2513(4)	77(2)
O(11)	-136(4)	751(3)	2649(2)	50(1)
O(12)	-95(5)	-1189(3)	2574(2)	79(2)
O(13)	999(4)	1818(3)	4024(2)	45(1)
O(14)	3315(6)	-1963(3)	6044(2)	95(2)
O(31)	437(4)	3928(3)	3048(2)	44(1)
O(32)	41(5)	5835(3)	3625(2)	76(2)
O(33)	-847(4)	2852(3)	2139(2)	43(1)
O(34)	-2553(7)	6623(3)	-13(2)	126(3)
N(11)	4143(5)	-20(4)	7089(2)	43(1)
N(12)	6133(6)	-647(4)	8300(2)	55(1)
N(13)	1954(5)	-1557(3)	4625(2)	45(1)
N(31)	-3466(5)	4665(4)	-1029(2)	41(1)
N(32)	-4092(5)	5343(4)	-2546(2)	48(1)
N(33)	-1516(5)	6236(3)	1471(2)	47(1)
C(11)	185(6)	-243(5)	2928(3)	45(2)
C(12)	888(6)	-274(4)	3708(3)	36(1)
C(13)	1246(6)	740(4)	4192(3)	33(1)
C(14)	1941(6)	536(4)	4936(3)	35(1)
C(15)	2315(6)	1478(4)	5464(3)	39(1)
C(16)	3007(6)	1237(4)	6143(3)	45(2)
C(17)	3391(6)	96(5)	6371(3)	42(1)
C(18)	5671(7)	321(5)	7118(3)	51(2)
C(19)	6333(7)	443(5)	7913(3)	60(2)
C(20)	6791(9)	-531(6)	9087(4)	105(3)
C(21)	4610(7)	-929(5)	8286(3)	57(2)
C(22)	3923(7)	-1103(5)	7495(3)	53(2)
C(23)	2988(7)	-836(5)	5854(3)	51(2)
C(24)	2266(8)	-2925(5)	5609(4)	79(2)
C(25)	2477(7)	-2752(4)	4823(3)	51(2)
C(26)	4007(9)	-2812(6)	4664(5)	116(3)
C(27)	1884(6)	-1372(4)	3958(3)	39(1)
C(28)	2284(6)	-609(4)	5140(3)	43(2)
C(31)	-40(6)	4906(5)	3240(3)	44(2)
C(32)	-720(6)	4944(4)	2444(3)	35(1)
C(33)	-1042(6)	3918(4)	1958(3)	36(1)
C(34)	-1655(6)	4130(4)	1202(3)	34(1)
C(35)	-2042(6)	3168(4)	681(3)	40(1)
C(36)	-2608(6)	3420(4)	-14(3)	40(1)
C(37)	-2857(6)	4568(5)	-284(3)	41(1)
C(38)	-2459(6)	4433(5)	-1599(3)	49(2)
C(39)	-3265(6)	4292(5)	-2371(3)	51(2)
C(40)	-4807(8)	5255(5)	-3306(3)	78(2)
C(41)	-5125(6)	5488(5)	-1993(3)	47(2)
C(42)	-4333(6)	5704(4)	-1208(3)	44(2)
C(43)	-2421(7)	5491(5)	224(3)	56(2)
C(44A)	-1279(11)	7415(8)	376(5)	49(4)
C(44B)	-3356(17)	7418(11)	743(8)	50(5)
C(45A)	-1620(50)	7370(30)	1140(20)	56(13)
C(45B)	-1900(40)	7550(30)	1261(17)	31(8)
C(46A)	-3170(20)	7759(9)	1286(7)	73(5)
C(46B)	-680(20)	7966(17)	904(10)	54(7)
C(47)	-1001(6)	6052(4)	2176(3)	42(1)
C(48)	-1879(6)	5280(4)	967(3)	43(2)
O(2)	9251(10)	411(6)	1050(4)	192(4)
O(3)	1851(7)	4361(4)	5045(3)	120(2)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

molecule. In addition two water molecules (shown in Fig. 4, pertinent crystallographic information given in Tables 2 and 3) provide additional crystalline stability through a network of hydrogen bond interactions.

### 3.4. Electronic spectra

The electronic spectra recorded in solid state and in aqueous solution of the Ni(II) complexes are similar,

suggesting the same chromophore in both states. A broad band is recorded at 650 nm ( $\epsilon = 12 \text{ M}^{-1} \text{ cm}^{-1}$ ), with a shoulder at 740 nm. This band is characteristic of regular or distorted octahedral structures; the main absorption is associated to transition  $\nu_2$  ( ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ ) and the shoulder to the spin-forbidden transition  ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ , which is usually recorded close to the main absorption, specially in complexes where  $\text{Dq}/\text{B}$  is close to 1, where the energies of states  ${}^3\text{T}_{1g}(\text{F})$  and  ${}^1\text{E}_g$  are very close [16,17]. Other bands

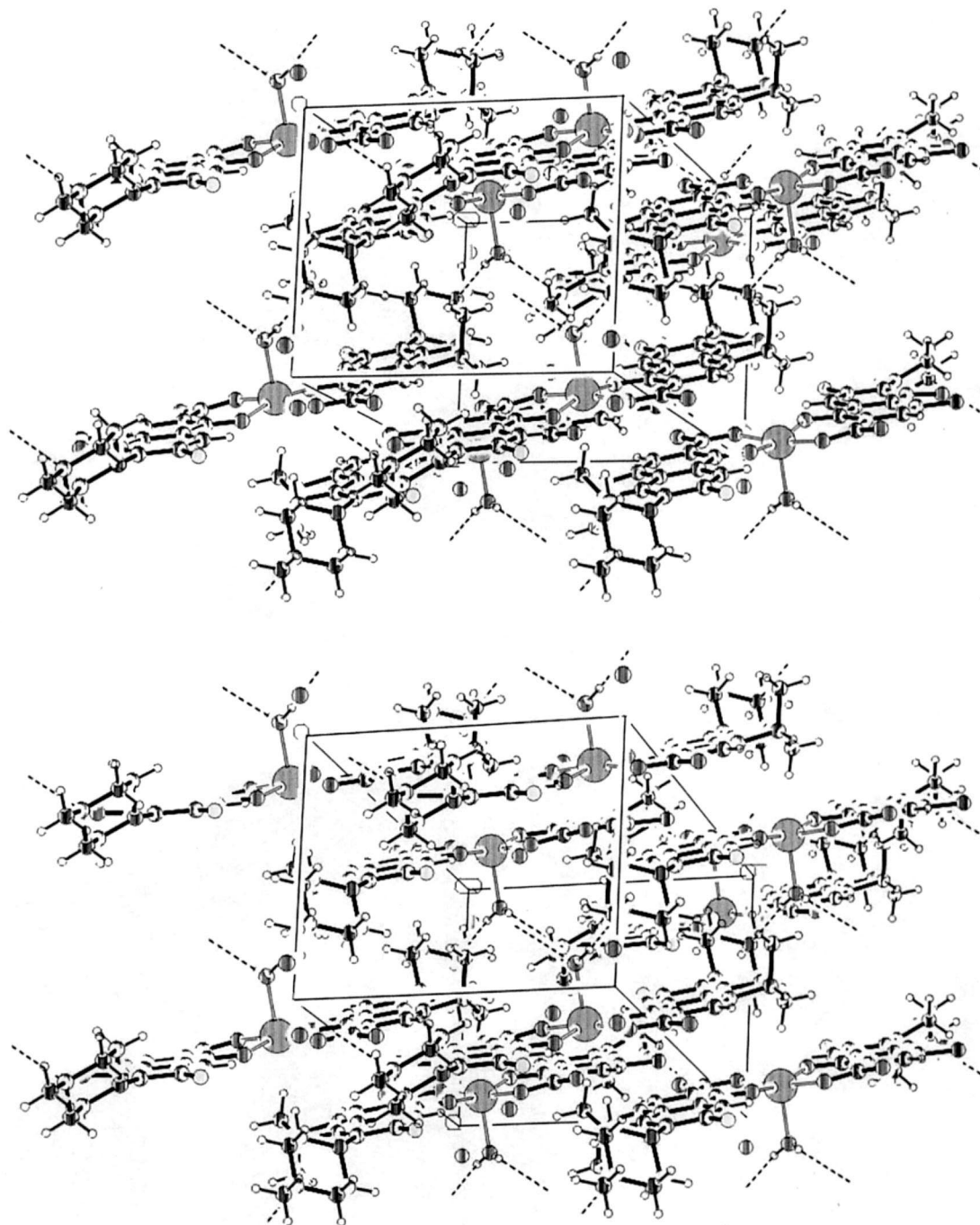


Fig. 4. Stereoscopic view of the unit cell showing the molecular packing and the intermolecular hydrogen bonding (dashed).

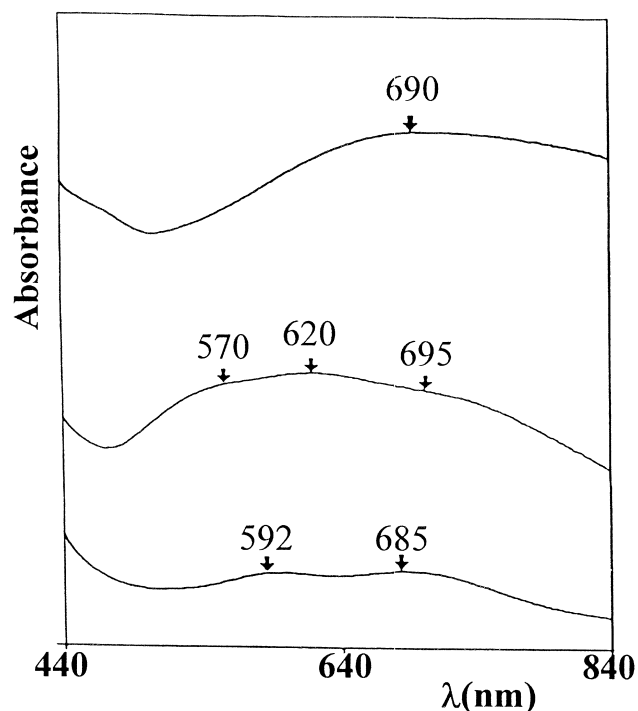


Fig. 5. Electronic spectra in the solid state for: (top)  $\text{Cu(olfo)Cl}\cdot 2.5\text{H}_2\text{O}$ ; (middle)  $\text{Cu(olfo)(NO}_3\text{)}\cdot 2.5\text{H}_2\text{O}$  and (bottom)  $\text{Cu(olfo)(SO}_4\text{)}_{0.5}\cdot 2.5\text{H}_2\text{O}$ .

in the ultraviolet region at 332, 290, and 258 nm ( $\epsilon = 35\,000\text{--}65\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) are due to transitions between energy levels of the ligands.

The solid spectra of the polymeric Cu(II) complexes (Fig. 5) show a broad asymmetric band with splittings that tentatively correspond to the splitting expected for the local  $\text{C}_{4v}$  symmetry of these cations in the square pyramidal geometry.

### 3.5. Magnetic susceptibility and EPR spectra

The magnetic moment measured at room temperature for the Ni complexes is similar in all cases, with  $\mu_{\text{eff}} = 3.12$  BM, which can be related to an octahedral (regular or distorted) environment [18]. The value measured is larger than the spin-only magnetic moment, 2.83 BM, and such an increase should be due to contributions from the orbital moment.

The value measured for the Cu complexes was  $\mu_{\text{eff}} = 1.98$  BM, also larger than the spin-only value, 1.73 BM. Such divergence is not uncommon in mononuclear Cu(II) complexes due to the mixing-in of some angular momentum from the closely lying excited states via spin-orbit coupling [19].

EPR spectroscopy is more sensitive to the chemical environment of the metal cation, and thus permits discrimination between the properties of the different complexes isolated, as shown in Fig. 6 for the Cu complexes. The

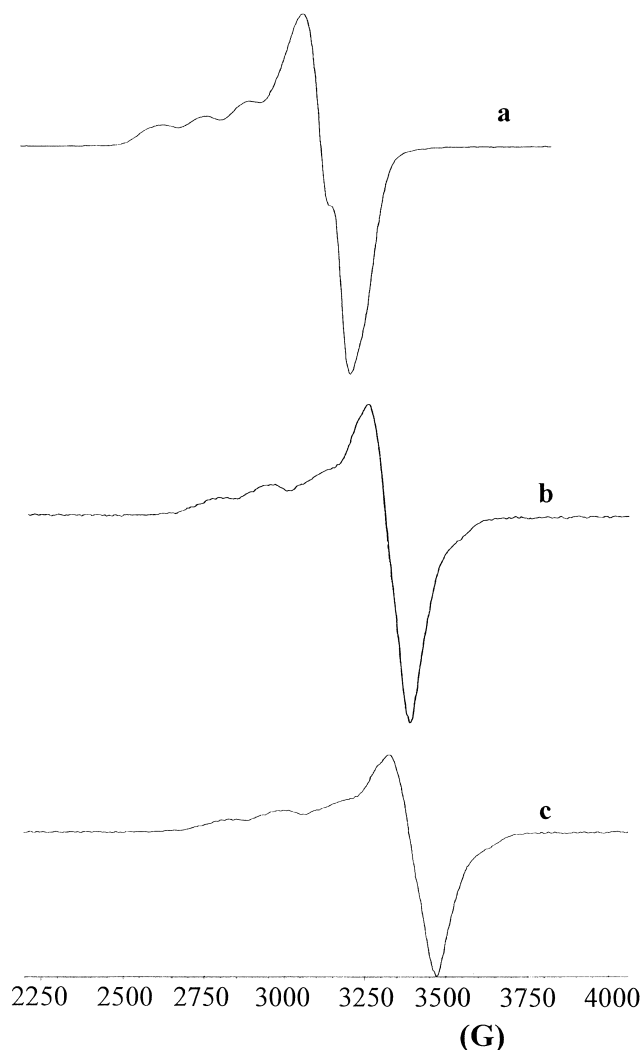


Fig. 6. EPR spectra for the compounds: (a)  $\text{Cu(olfo)Cl}\cdot 2.5\text{H}_2\text{O}$ ; (b)  $\text{Cu(olfo)(SO}_4\text{)}_{0.5}\cdot 2.5\text{H}_2\text{O}$  and (c)  $[\text{Cu(olfo)}_2\cdot \text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ .

EPR values was obtained by simulation [20]. The EPR spectrum of polycrystalline  $\text{Cu(olfo)Cl}\cdot 2.5\text{H}_2\text{O}$  complex were  $g_1 = 2.11$ ,  $g_2 = 2.17$ ,  $g_3 = 2.41$  and  $A_{\parallel} = 150$  G, rather close to those reported for a square base pyramid structure [21]. The value for the  $R$  parameter [ $R = (g_2 - g_1)/(g_3 - g_2)$ ] is 0.25, i.e. lower than 1, thus indicating that the unpaired electron is located in orbital  $dx^2 - y^2$ . The EPR spectrum of the  $\text{Cu(olfo)(SO}_4\text{)}_{0.5}\cdot 2.5\text{H}_2\text{O}$  is axial slightly rhombic with  $g$  parameters according to the simulation programme,  $g_1 = 2.04$ ,  $g_2 = 2.07$ ,  $g_3 = 2.27$  and  $A_{\parallel} = 170$  G. Finally, the values for the crystalline complex  $[\text{Cu(olfo)}_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  were  $g_{\parallel} = 2.22$ ,  $g_{\perp} = 2.00$  and  $A_{\parallel} = 160$  G, very close to those reported in the literature for a square base pyramid structure, in agreement with the structure concluded for this complex from the XRD data discussed above (Fig. 3). Nevertheless, according to all these data, the local geometry around copper should be close to tetragonal in all cases.

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