

Crystal and molecular structure and spectroscopic properties of diaquabis(*N*-acetyl-*D,L*-phenylglycinato)bis(imidazole)copper(II)

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Abstract

The diaquabis(*N*-acetyl-*D,L*-phenylglycinato)bis(imidazole)copper(II) compound has been prepared and structurally and spectroscopically characterized. The structure consists of monomeric units, in which the copper atom presents a tetragonally distorted octahedral coordination with two centrosymmetrically related carboxyl oxygens and imidazole nitrogen atoms in the square plane. Two long contacts in the out-of-plane axial positions, involving the two water molecules, complete the coordination, giving rise to a $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophore. In the imidazole adducts of the copper(II) compounds of the *N*-substituted amino acids the metal(II) ion was until now found in an essentially square-planar geometry with a CuN_2O_2 chromophore. Magnetic and spectroscopic results also confirm a tetragonally distorted octahedral coordination geometry of the copper(II) ion with $(xy)^2(xz,yz)^4(z^2)^2(x^2-y^2)$, 2A_g (C_i symmetry) ground state.

Introduction

It is known that low-molecular-weight ternary complexes of copper(II), in which a mixed N,O-atom donor set is the preferred chromophore [1, 2], are abundant in living systems, being involved in the transport of metal ions through biological fluids and living tissues. Comparative studies on small synthetic systems duplicating these metal ion arrangements have indicated that their relatively high stability is primarily responsible for the large range of natural occurrence of mixed complexes. The major contribution to their stability derives from the presence of an imidazole moiety in the metal coordination sphere enabling π -backdonation from metal to unsaturated ligand p-orbitals lowering the electron concentration near the central ion [3].

Ternary copper(II)/*N*-substituted-amino acid/imidazole systems provide many closely related structural and spectroscopic data, which reproduce realistic model systems of many naturally occurring mixed ligand complexes. The resultant effect of the basic properties ($\text{p}K_A$ about 7.0) and π -backdonation power of imidazoles always leads to separate complexes in which the copper(II) ion geometry is found to be essentially square

planar with a *trans*- CuN_2O_2 chromophore [4–6]. In these complexes the involvement of the second carboxylic oxygen atom and of the water (or alcoholic) molecules, if present, in the metal ion coordination can be invariably excluded, and these groups are only involved in hydrogen bonding as part of the presumably crystal packing [5–7].

Being particularly interested in this field we discuss here the structural and spectroscopic results of the diaquabis(*N*-acetyl-*D,L*-phenylglycinato)bis(imidazole)-copper(II) (hereafter abbreviated as $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$, where *ac-phglyO* = *N*-acetyl-*D,L*-phenylglycinate ion; *im* = imidazole), which presents a bonding arrangement unusual for copper(II)-*N*-substituted amino acid-imidazole compounds.

Experimental

Preparation of the $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$ compound

By mixing copper(II) acetate dihydrate (1 mmol) and *N*-acetyl-*D,L*-phenylglycine (2 mmol) in methanol, followed by slow evaporation of the solution, a micro-

crystalline compound of formula bis(*N*-acetyl-D,L-phenylglycinato)copper(II) separates out after some days. This compound reacts with imidazole (in 1:1 or 1:2 molar ratio) in a water/ethanol (1:1) solution, producing deep blue crystals suitable for X-ray analysis. *Anal.* Calc. for $C_{26}H_{32}CuN_6O_8$: C, 50.4; H, 5.2; N, 13.5. Found: C, 50.5; H, 5.3; N, 13.4%.

Physical measurements

Thermogravimetric analysis was performed with a Dupont 1090 thermal analyzer and differential scanning calorimetric analysis with a Perkin-Elmer DSC-2C calorimeter equipped with an IBM PS 2/30 automatic data acquisition and processing soft-ware, employing sealed Al pans.

The diffuse reflectance electronic spectrum of the solid powdered compound was recorded on a DK2A-Beckman spectrophotometer (BaSO₄ as reference).

IR spectra were performed on KBr pellets of the sample in the spectral range 4000–500 cm⁻¹ and on polyethylene pellets in the spectral range 500–100 cm⁻¹ with a Digilab FTS 40 spectrophotometer.

The FT-Raman spectrum was obtained on a solid sample in the spectral range 3500–100 cm⁻¹ using a Bruker FRA-106 spectrophotometer equipped with an Nd-YAG laser.

The room temperature magnetic moment was measured by the Faraday method using a Cahn-Ventron apparatus and was corrected for diamagnetism with the appropriate Pascal constants.

The EPR spectrum was recorded on an X-band Varian E9 spectrometer.

X-ray structure determination

A crystal of approximate dimensions 0.26 × 0.16 × 0.39 mm was mounted on a Siemens AED single crystal diffractometer using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at a temperature of 293 K. Crystal data and parameters associated with data collection are summarized in Table 1. The lattice parameters were determined from least-squares refinement of θ values of 15 reflections accurately measured. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by Patterson and Fourier methods and refined isotropically and anisotropically by least-squares. The hydrogen atoms, located in the final ΔF map, were included in the last cycle of refinement. The atomic scattering factors for the neutral atoms were taken from ref. 8. The final atomic coordinates for the non-hydrogen atoms are reported in Table 2. For anisotropic and isotropic thermal parameters, coordinates of hydrogen atoms and observed and calculated structure factors see 'Supplementary material'. All calculations were performed on a GOULD 32/77 computer of the Centro di Studio per la Strut-

TABLE 1. Crystal data for [Cu(ac-phglyO)₂(im)₂(H₂O)₂]

Compound	Cu(ac-phglyO) ₂ (im) ₂ (H ₂ O) ₂
Formula	C ₂₆ H ₃₂ CuN ₆ O ₈
Molecular weight	620.12
Space group	P $\bar{1}$
<i>a</i> (Å)	10.156(7)
<i>b</i> (Å)	9.488(6)
<i>c</i> (Å)	8.452(3)
α (°)	84.45(3)
β (°)	93.39(3)
γ (°)	63.55(3)
<i>V</i> (Å ³)	721(7)
<i>Z</i>	1
<i>D</i> _{calc} (g cm ⁻³)	1.43
<i>D</i> _{obs} (by flotation) (g cm ⁻³)	1.42
<i>F</i> (000)	323
μ (cm ⁻¹)	15.24
θ Range (°)	3–70
Scan mode	ω -2 θ
No. measured reflections	2305
No. reflections used	1794
Condition of observed reflections	$I > 2\sigma(I)$
No. refined parameters	251
$R = \Sigma F /\Sigma F_o $ (%)	5.8
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$ (%)	6.1
<i>k</i> , <i>g</i> ($w = k/[\sigma^2(F_o) + g(F_o)^2]$)	1.0, 0.020721

TABLE 2. Fractional atomic coordinates for [Cu(ac-phglyO)₂(im)₂(H₂O)₂]

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	0(0)	0(0)	0(0)
O(1)	0.0865(2)	0.1449(2)	0.0264(3)
O(2)	0.3174(3)	0.0063(3)	-0.0290(3)
O(3)	0.2607(3)	0.5303(3)	-0.0993(4)
N(1)	0.3665(4)	0.2673(4)	-0.0279(4)
N(2)	-0.1046(3)	0.1307(3)	-0.2085(3)
N(3)	-0.1904(5)	0.1921(6)	-0.4607(7)
C(1)	0.2154(3)	0.1245(3)	0.0096(3)
C(2)	0.2415(4)	0.2667(4)	0.0463(4)
C(3)	0.2561(4)	0.2651(4)	0.2259(4)
C(4)	0.1307(8)	0.3142(7)	0.3058(8)
C(5)	0.1454(9)	0.2993(8)	0.4730(8)
C(6)	0.2831(10)	0.2404(9)	0.5580(7)
C(7)	0.4028(9)	0.1976(9)	0.4807(7)
C(8)	0.3931(6)	0.2080(7)	0.3145(6)
C(9)	0.3665(4)	0.3987(4)	-0.0994(4)
C(10)	0.5016(5)	0.3812(6)	-0.1770(5)
C(11)	-0.1306(5)	0.0761(5)	-0.3376(5)
C(12)	-0.2044(5)	0.3287(6)	-0.4123(6)
C(13)	-0.1504(4)	0.2899(5)	-0.2551(6)
OW	-0.2220(6)	0.1715(5)	0.2052(6)

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Results and discussion

The compound is stable in air and soluble in polar organic solvents. The TG analysis demonstrates a weight

loss of about 6% between 63 and 92 °C, which is in good agreement with the calculated value (5.8%) for the complete loss of both water molecules. The heat of transformation ($\Delta H = 28.5$ Kcal/mol), measured by means of differential scanning calorimetric analysis, agrees very well with the dehydration heat for the loss of one mole of water molecule ($\Delta H = 12.8\text{--}14$ Kcal/mol H_2O) in the crystal hydrates [11, 12].

Description of the structure (Fig. 1)

The structure consists of monomeric units in which the copper atom presents a tetragonally elongated octahedral configuration with two centrosymmetrically related carboxyl oxygens and imidazole nitrogen atoms in the square plane. Two long contacts in the out-of-plane axial positions, involving the two water molecules, complete the coordination. The most relevant bond distances and angles are reported in Table 3. The N-substituted amino acid coordination strictly resembles that normally reported for binary and ternary N-substituted amino acid copper(II) complexes, in which the carboxylic group behaves as an essentially unidentate ligand [3, 4–7], with a Cu–O distance of 1.956(3) Å which is also in the range of those generally observed in carboxylate complexes [13].

In our complex it is particularly worth noting the presence of coordinated water molecules. In fact in all the imidazole adducts of copper(II) N-substituted amino acids (where the substituting group is an acetyl or a benzoyl group) investigated up to now, the copper(II) ion presents an essentially square-planar geometry with a CuO_2N_2 chromophore [4, 7, 14] and the water molecules, if present, were never found involved in the metal ion coordination. In these compounds the coordination of the water molecules appears to be strongly hindered by the second carboxylic oxygen atom, which, although positioned at a distance from the metal ion

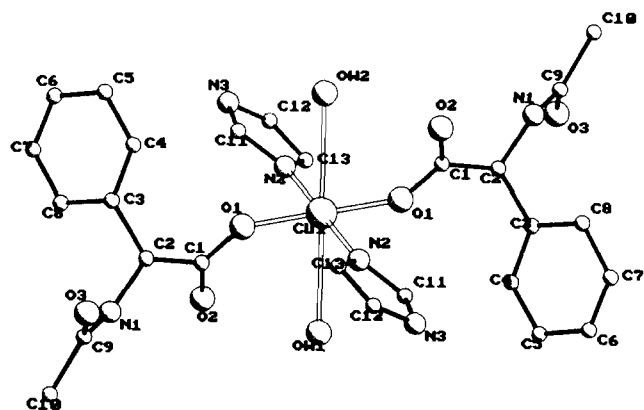


Fig. 1. Projection of the structure of $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$ with the numbering scheme.

TABLE 3. Bond distances (Å) and angles (°) of $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$

Cu–O(1)	1.956(3)	Cu–N(2)	1.989(3)
Cu–OW	2.912(5)		
O(1)–C(1)	1.254(5)	O(2)–C(1)	1.230(4)
O(3)–C(9)	1.233(4)	N(1)–C(2)	1.451(7)
N(1)–C(9)	1.332(6)	N(2)–C(11)	1.314(6)
N(2)–C(13)	1.375(6)	N(3)–C(11)	1.331(7)
N(3)–C(12)	1.347(9)	C(1)–C(2)	1.542(6)
C(2)–C(3)	1.514(5)	C(3)–C(4)	1.389(9)
C(3)–C(8)	1.384(7)	C(4)–C(5)	1.398(9)
C(5)–C(6)	1.375(12)	C(6)–C(7)	1.333(12)
C(7)–C(8)	1.393(7)	C(9)–C(10)	1.505(7)
C(12)–C(13)	1.356(7)		
O(1)–Cu–N(2)	88.4(2)	Cu–O(1)–C(1)	129.1(3)
C(2)–N(1)–C(9)	123.3(4)	Cu–N(2)–C(13)	128.8(3)
Cu–N(2)–C(11)	125.6(3)	C(11)–N(2)–C(13)	105.3(4)
C(11)–N(3)–C(12)	109.1(5)	O(1)–C(1)–O(2)	127.1(4)
O(2)–C(1)–C(2)	119.7(4)	O(1)–C(1)–C(2)	113.1(4)
N(1)–C(2)–C(1)	111.4(4)	C(1)–C(2)–C(3)	108.7(3)
N(1)–C(2)–C(3)	113.6(4)	C(2)–C(3)–C(8)	121.4(4)
C(2)–C(3)–C(4)	119.8(5)	C(4)–C(3)–C(8)	118.7(5)
C(3)–C(4)–C(5)	119.7(7)	C(4)–C(5)–C(6)	120.3(7)
C(5)–C(6)–C(7)	119.8(6)	C(6)–C(7)–C(8)	121.7(8)
C(3)–C(8)–C(7)	119.7(6)	O(3)–C(9)–N(1)	121.1(4)
N(1)–C(9)–C(10)	117.7(4)	O(3)–C(9)–C(10)	121.2(4)
N(2)–C(11)–N(3)	110.6(5)	N(3)–C(12)–C(13)	105.2(5)
N(2)–C(13)–C(12)	109.8(4)		

of about 2.74–2.91 Å, forms an angle with the normal to square coordination plane of 36–41° which prevents overlap of the metal–ligand orbitals [5, 6]. In the present compound the Cu–OH₂ distances of 2.912(5) Å (axial bonding interactions to the copper(II) ion are considered up to 3.3 Å [15]) and the angle with the normal to the coordination plane of 8.6(2)° suggest the presence of a $\text{CuN}_2\text{O}_2\text{O}'_2$ chromophore. The global view of the structural and spectroscopic results for some anhydrous and hydrated ternary N-substituted amino acid copper(II) with imidazoles, collected in Table 4, agree with the statements given above.

The Cu–N(2) bond length of 1.989(3) Å resembles those found in most Cu^{2+} –imidazole compounds (about 2.00 Å) [16] more than those reported for oligoglycines– Cu^{2+} –imidazole complexes (1.95 Å) and for similar compounds (as those collected in Table 4) (1.959(5)–1.976(6) Å). This suggests in the compound under study, with respect to the similar imidazole compounds reported in Table 4, a slight decrease of π -backbonding interactions between the copper(II) ion and the heteroatomic N bases, as a consequence of the introduction of water molecules into the coordination sphere.

The structure of $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$ is very similar to those found in similar ternary complexes with amines of lower basicity, such as pyridines, in which the copper(II) ion can achieve octahedral geometry,

TABLE 4. Correlation between Cu...O axial distances (Å), normal to bipyramidal distortion angles^a (°) and d-d band maximum (cm⁻¹)

Compound ^b	Cu...O _{ax}	Angle ^a band max.	d-d	Chromophore	Ref.
[Cu(ac-phglyO) ₂ (im) ₂ (H ₂ O) ₂]	2.912(5)	8.6	13.3	N ₂ O ₂ O' ₂	
[Cu(bz-glyO) ₂ (im) ₂]	2.736(4)	37.2	17.5	N ₂ O ₂	4
[Cu(ts-glyO) ₂ (meim) ₂]	2.758(4)	37.8	17.9	N ₂ O ₂	14
[Cu(ts-β-alaO) ₂ (im) ₂]	2.761(5)	36.8	18.2	N ₂ O ₂	7
[Cu(ac-α-alaO) ₂ (meim) ₂]·2H ₂ O	2.907(4)	41.1	18.2	N ₂ O ₂	5
[Cu(z-β-alaO) ₂ (meim) ₂]·C ₂ H ₅ OH	2.731(5)	36.4	17.6	N ₂ O ₂	6
[Cu(ac-trphO) ₂ (py) ₂ (H ₂ O) ₂]	2.61(1)	2.7	15.9	N ₂ O ₂ O' ₂	17

^aAngle between the Cu...O axial vector and the normal to the coordination plane. ^bAbbreviations: bz-glyO: *N*-benzoylglycinate ion; ts-glyO: *N*-tosylglycinate ion; ts-β-alaO: *N*-tosyl-β-alanine ion; ac-α-alaO: *N*-acetyl-α-alanine ion; z-β-alaO: *N*-benzyloxycarbonyl-D,L-alanine ion; ac-trphO: *N*-acetyl-D,L-tryptophan ion.

since the lowering of the in-plane ligand field donor in respect to the imidazole adducts favours the axial coordination of water molecules [17–19]. In this compound the presence of a phenyl group in α position on the amino acid seems to play an important role in favouring water coordination since it may sterically or hydrophobically perturb the imidazole coordination.

The copper atom lies 0.163 Å out of the imidazole plane. The C^αCOO-group is planar with the peptidic nitrogen 0.492 Å out of the plane, nearly perpendicular to the phenyl group and the imidazole molecule, while it forms an angle of 38° with the peptidic group. The imidazole molecule is nearly normal to the phenyl ring (81.8°). In the glycinate moiety the conformation is described by the torsion angles around the C–N and C–C bonds (C(9)–N(1)–C(2)–C(1) = 138.6(4)°; O(1)–C(1)–C(2)–N(1) = –158.9(4)°) which indicate that the amino acid is in the extended form.

Packing (see Fig. 2) is mainly determined by an extended network of hydrogen bonding interactions (Table 5) which involve intramolecularly the water molecules and the second carboxylic oxygen atom and intermolecularly the water molecules with the peptidic oxygen atoms along the [010] axis and the imidazole NH group along the [001] axis. Finally the peptidic nitrogen atom connects the structure along the [100] axis with interactions between the nitrogen atom and the second carboxylic oxygen atom. No stacking interactions are observed between hydrophobic moieties of the amino acids.

Spectroscopic and magnetic results

The [Cu(ac-phglyO)₂(im)₂(H₂O)₂] compound displays the magnetic ($\mu_B = 1.88$ bm at room temperature) and spectral (one broad d–d band centred at 13 300 cm⁻¹) characteristics of a tetragonally distorted octahedral metal ion geometry with $(xy)^2(xz,yz)^4(z^2)^2(x^2-y^2)$, ²A_g (C₄ symmetry) ground state, with a CuN₂O₂O'₂ chromophore [17, 20, 21] analogous to that observed for the

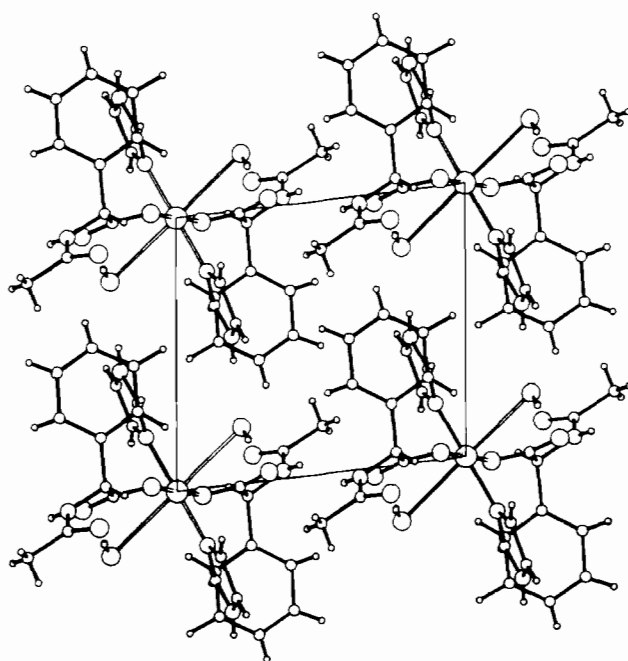


Fig. 2. Crystal packing of [Cu(ac-phglyO)₂(im)₂(H₂O)₂].

TABLE 5. Hydrogen bonding interactions in [Cu(ac-phglyO)₂(im)₂(H₂O)₂] (distances (Å) and angles (°))

OW...O(3) ⁱ	2.728(6)	OW–H(1)W	0.79(7)
H(1)W...O(3) ⁱ	1.97(7)	OW–H(1)W...O(3) ⁱ	160
OW...O(2) ⁱⁱ	2.788(7)	OW–H(2)W	0.63(7)
H(2)W...O(2) ⁱⁱ	2.17(7)	OW–H(2)W...O(2) ⁱⁱ	173
N(3)...OW ⁱⁱⁱ	2.859(8)	N(3)–H(9)	0.81(4)
H(9)...OW ⁱⁱⁱ	2.08(4)	N(3)–H(9)...OW ⁱⁱⁱ	161
N(1)...O(2) ^{iv}	3.070(5)	N(1)–H(7)	0.77(4)
H(7)...O(2) ^{iv}	2.43(3)	N(1)–H(7)...O(2) ^{iv}	140

i = –x, 1–y, –z; ii = –x, –y, –z; iii = x, y, z–1; iv = 1–x, –y, –z.

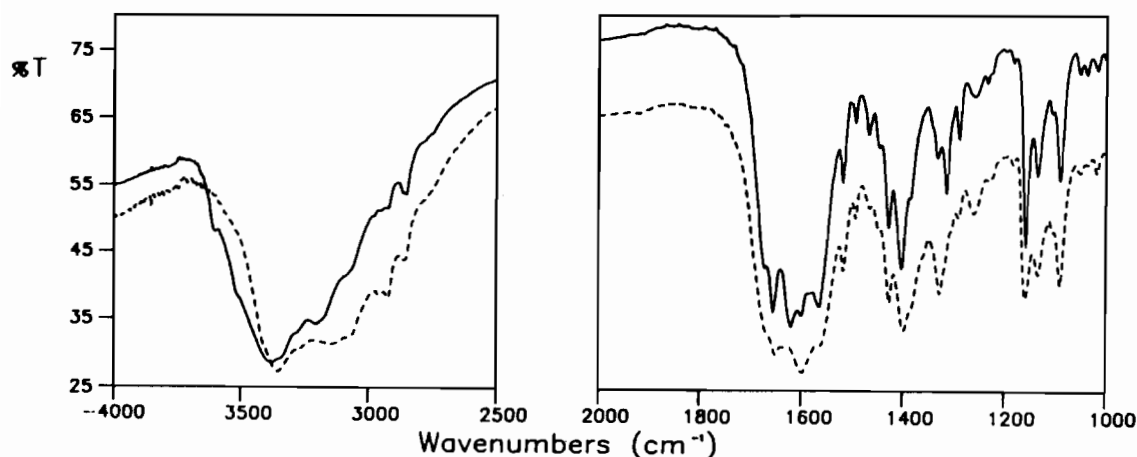


Fig. 3. IR spectra of KBr pellets of $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$; —, untreated compound; ---, dehydrated compound.

TABLE 6. Frequencies of metal–ligand stretching vibrations (cm^{-1})^a of $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$

Frequencies	Assignment	Infrared (IR) Raman (R)	Reference
333w	$\nu(\text{Cu-O})$, water	IR	20
317w	$\nu(\text{Cu-O})$	IR	20
296m	$\nu(\text{Cu-N})$	IR	22, 23
284m	$\nu(\text{Cu-N})$	R	

^aw = weak, m = medium.

TABLE 7. Selected IR and Raman spectra (cm^{-1}) of $[\text{Cu}(\text{ac-phglyO})_2(\text{im})_2(\text{H}_2\text{O})_2]$

Frequencies	Approximate description of vibration	Infrared (IR) Raman (R)	Reference
3588sh	$\nu_{\text{as}}(\text{OH}_2)$	IR	
3500sh	$\nu_s(\text{OH}_2)$	IR	
3354vs	$\nu(\text{NH})$, amide	IR	20
3283sh	$\nu(\text{NH})$, imidazole	IR	24, 25
3210sh	overtone H_2O bending	IR	
1651vs	$\nu(\text{CO})$, amide	IR	20
1622vs	H_2O bending	IR	20
1623vs	H_2O bending	R	
1599vs	$\nu_{\text{as}}(\text{CO}_2)$	R	
1598vs	$\nu_{\text{as}}(\text{CO}_2)$	IR	20
1418vs	$\nu_s(\text{CO}_2)$	R	
1404vs	$\nu_s(\text{CO}_2)$	IR	20
1209s	NH bending, imidazole	R	26

structurally similar diaquabis (*N*-acetyl-*DL*-tryptophanato)bis(pyridine)copper(II) compound [17]. The higher d-d band value for this latter compound (15.9 cm^{-1}) is consistent with the lower axial Cu-OH₂ distance ($2.61(1) \text{ \AA}$).

The vibrational analysis of the skeletal stretching vibrations has been conducted on the basis of the C_i point group symmetry, which represents both the site symmetry of the copper atom and the factor group of the molecule in the crystal. As regards $\nu(\text{Cu-O})$ and $\nu(\text{Cu-N})$ vibrations, we calculated one Raman active A_g symmetric stretching and one IR active A_u asymmetric stretching (see Table 6).

The water vibrational bands, assigned by comparing the IR spectrum of the untreated compound with the spectrum of the heated compound at 100°C (see Fig. 3) are reported in Table 7, which also contains the vibrational bands of imidazole and of the functional groups.

Supplementary material

Listings of anisotropic and isotropic thermal parameters, coordinates of hydrogen atoms and observed and calculated structure factors (15 pages) are available for the authors on request.

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