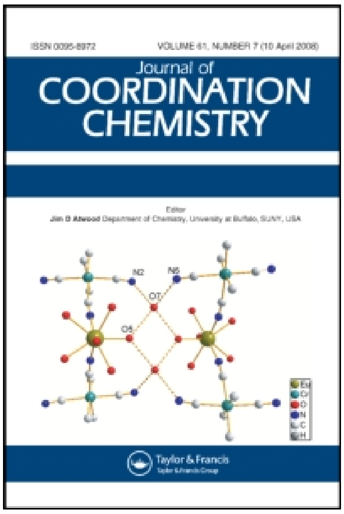

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Synthesis and characterization of some new mono- and binuclear copper(II) ternary complexes; X-ray crystal structure of copper(II)-<i>N</i>-(acetyl)phenylglycinate-imidazole ternary complex

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Synthesis and characterization of some new mono- and binuclear copper(II) ternary complexes; X-ray crystal structure of copper(II)-*N*-(acetyl)phenylglycinate–imidazole ternary complex

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A series of new copper(II) ternary complexes with *N*-(benzoyl)leucinate and *N*-(acetyl)phenylglycinate and certain N-heterocyclic ligands (quinoxaline, 2,4,6-tris-(2-pyridyl)-1,3,5-triazine and oxalic acid diimidazolide) have been synthesized and characterized by elemental analysis, IR and EPR spectra as well as thermogravimetric analysis. The structure of *bis*-(*N*-(acetyl)phenyl-glycinato)-*bis*-(imidazole)copper(II) was also characterized by X-ray single crystal analysis. The structure consists of monomeric units, in which the copper atom exists in a square-planar geometry with a CuN_2O_2 chromophore with two centrosymmetrically related carboxyl oxygens and imidazole nitrogen atoms.

Keywords: Copper; *N*-(benzoyl)leucine; *N*-(acetyl)phenylglycine; Nitrogen heterocyclic compounds; Binuclear ternary complexes; EPR

1. Introduction

Copper proteins containing mono-, di-, tri- or multinuclear centers are important in biology [1–4]. Copper ions are found in the active sites of a large number of metalloproteins involved in important biological electron-transfer reactions and in redox processes of molecular oxygen [5]. Copper complexes with ligands containing pyridine, imidazole and pyrazole derivatives have been prepared to study their molecular structures and/or their function modeling copper-containing enzymes such as superoxide dismutases, blue copper oxidases and tyrosinase [1, 6]. Also, binuclear copper-containing proteins play an important role in biology, including dioxygen transport or activation, electron transfer, reduction of nitrogen oxides and hydrolytic chemistry. In physicochemical aspects binuclear copper complexes have significance as new inorganic materials with various magnetic properties [7]. Notable advances in understanding structural and chemical properties of copper proteins have been achieved through comparison of sythestic models to the naturally occurring molecules [8–10].

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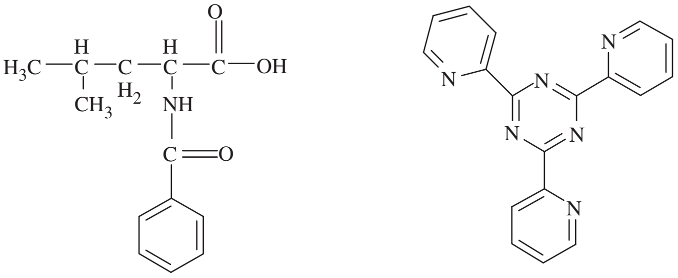
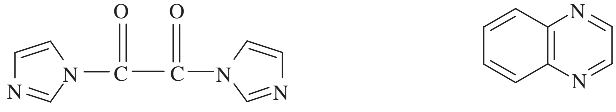


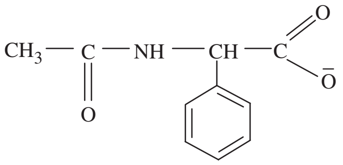
N-(benzoyl)leucine (bz-leu)

2,4,6-Tris-(2-pyridyl)-1,3,5-triazin (py-triaz)



Oxalic acid diimidazolide (oximid)

Quinoxaline (qox)



N-(acetyl)phenylglycinate (Ac-phgly)

Scheme 1. The structure of ligands.

In this article, we report the synthesis and characterization of some novel mono- and binuclear Cu(II) complexes of *N*-(benzoyl)leucinate and *N*-(acetyl)phenylglycinate with a series of N-heterocyclic ligands such as imidazole, quinoxaline, 2,4,6-tris-(2-pyridyl)-1,3,5-triazine and oxalic acid diimidazolide (scheme 1). The structure of *bis*-(*N*-(acetyl)phenylglycinato)-*bis*-(imidazole)copper(II) was characterized by X-ray single crystal structural analysis. Electron paramagnetic studies of the binuclear Cu(II) complexes are also discussed.

2. Experimental

2.1. *Materials*

All chemicals were of the highest purity commercially available. All solvents were purified by distillation according to standard methods.

2.2. *Synthesis of complexes*

2.2.1. Syntheses of $[Cu_2(qox)_2(bz\text{-}leu)_4]$, $[Cu_2(OH)_2(H_2O)_2(py\text{-}triaz)(bz\text{-}leu)_2] \cdot 4H_2O$ and $[Cu(oximid)(bz\text{-}leu)_2]$ complexes. To a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.12 g, 0.50 mmol) and either quinoxaline (0.065 g, 0.50 mmol), 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (0.16 g, 0.50 mmol) or oxalic acid diimidazolide (0.095 g, 0.50 mmol) in methanol, an aqueous solution of *N*-(benzoyl)leucine (0.12 g, 0.50 mmol) was added dropwise with stirring. The pH of the solution was then adjusted to 8 using concentrated aqueous NaOH. The solid complexes were separated by slow evaporation.

2.2.2. Synthesis of [Cu(imi)$_2$(Ac-phgly)$_2$] · H$_2$O. The [Cu(imi)$_2$(Ac-phgly)$_2$] · H_2O complex was prepared by mixing copper(II) acetate (2.0 mmol in 20 cm^3) and *N*-(acetyl)phenylglycinate (2.0 mmol in 20 cm^3) in a 1 : 1 methanol–water mixture, followed by addition of a methanolic solution of imidazole (4.0 mmol in 10 cm^3). The mixture was refluxed for 2 h and left covered for nearly 3 weeks at which time a dark blue crystalline material was deposited.

2.3. *Instrumentation*

Elemental CHN analyses were carried out on a Carlo-Erba EA1108 elemental analyzer. Infrared spectra (KBr pellets) were performed on a Nicolet 5PC FT–IR spectrometer. Thermogravimetric (TG) analyses were carried out under nitrogen with a heating rate of 10°C min^{-1} using a Stanton STA 1500 Thermal analyzer. Electron paramagnetic resonance spectra were obtained at room temperature in the X-band using a Varian X-Band Spectrometer model E-109.

2.4. *X-ray data collection and structure refinement*

The X-ray diffraction data for the [Cu(imi)$_2$(Ac-phgly)$_2$] · H_2O were collected at room temperature on a maXus (Bruker Nonius, Delft & Mac Science, Japan) using Mo-Kα radiation. A standard reflection was monitored every 100 reflections, during the data collection process, without significant variations. The structure was solved with *SIR*92 [11] and the refinements were carried out with maXus [12]. For the present structure most hydrogen atoms were found in a final ΔF map, the remaining hydrogen atoms were put in their theoretical positions and refined automatically. The crystal data and relevant details concerning data collection and refinements are summarized in table 3. The projection of the complex, in which the ellipsoids are at 30% probability level, is in figure 4 [13–15].

3. Results and discussion

3.1. *IR spectra*

The IR spectra of the complexes exhibited the characteristic bands of the ligands with the corresponding shifts due to complex formation (table 2). The IR spectra of [Cu$_2$(OH)$_2$(H$_2$O)$_2$(py-triaz)(bz-leu)$_2$] · 4H_2O and [Cu(imi)$_2$(Ac-phgly)$_2$] · H_2O displayed a broad band in the range 3507–3457 cm^{-1}, ascribed to stretching vibrations of water present in either the lattice or coordinated to the metal consistent with elemental and TG analyses. In addition, the IR spectra of all complexes showed a distinct strong band in the range 3420–3300 cm^{-1} corresponding to the stretching vibration of the NH

Table 1. Analytical data, melting points and electrical conductance for the copper(II) complexes.

Complex	Fw	Found (Calcd)% C	H	N	Mp (°C)	Ω (μS)
$[Cu_2(quinox)_2(bz\text{-}leu)_4]$	1328.5	61.26 (61.42)	5.57 (6.02)	8.56 (8.43)	216	28
$[Cu_2(OH)_2(H_2O)_2(2\text{-}py\text{-}triazin)(bz\text{-}leu)_2]\cdot 4H_2O$	1017.94	51.83 (51.83)	5.24 (5.89)	11.27 (11.00)	250	33
$[Cu(oxalimid)(bz\text{-}leu)_2]$	724.26	56.24 (56.33)	5.96 (5.52)	11.89 (11.60)	188	31
$[Cu(imi)_2(Ac\text{-}phgly)_2]\cdot H_2O$	620.12	50.11 (50.15)	5.04 (5.14)	13.36 (13.50)	185	38

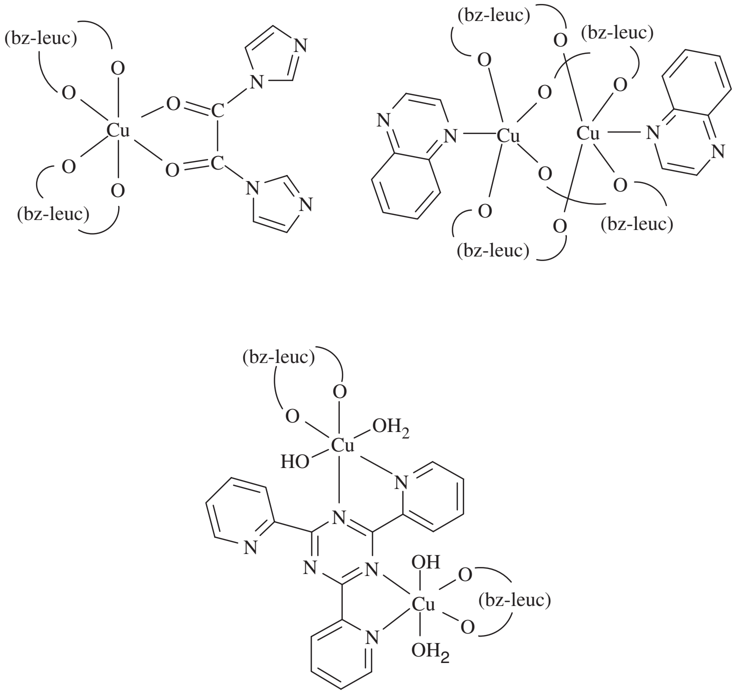
Table 2. Important IR data for the copper(II) complexes.

Complex	$\nu(OH)$	$\nu(NH)_{imi}$	$\nu(CO)_{ket}$	$\nu(COO)_{as}$	$\nu(COO)_s$	$\Delta\nu$
$[Cu_2(quinox)_2(bz\text{-}leu)_4]$	–	3348sh	1631s	1581sh	1411s	170
$[Cu_2(OH)_2(H_2O)_2(py\text{-}triaz)(bz\text{-}leu)_2]\cdot 4H_2O$	3507sh	3420sh	1635s	1604s	1448m	156
$[Cu(oxalimid)(bz\text{-}leu)_2]$	–	3434m	1632s	1600sh	1482m	118
$[Cu(imi)_2(Ac\text{-}phgly)_2]\cdot H_2O$	3495sh	3308s	1631m	1597s	1384s	213

group, $\nu(NH)_{amid}$, of *N*-(benzoyl)leucinate or *N*-acetyl(phenylglycinate). IR spectra of all complexes also exhibited a strong band in the range 1638–1631 cm^{-1} assigned to the stretching vibration of the amide carbonyl groups, $\upsilon(CO)_{amid}$. The presence of a strong band in the range of 1605–1581 cm^{-1} in the IR spectra of all complexes (table 2), typical for asymmetric vibration of coordinated carboxylate, confirmed the coordination of the *N*-(benzoyl)leucinate and *N*-(acetyl)phenylglycinate ligands through the carboxylate oxygen [16, 17]. The band at 1482–1411 cm^{-1} from the symmetric vibration of the coordinated carboxylate gives a frequency difference ($\Delta\upsilon$ values) of 118–170 cm^{-1} for *N*-(benzoyl)leucinate complexes confirming the bidentate mode of the carboxylate. The electrical molar conductance in DMSO at room temperature lies in the 28–38 μS range, which indicates that the reported complexes are nonelectrolytes with the ligand anion coordinated to the copper. According to elemental analysis and spectroscopic studies, the complexes have the structures shown in scheme 2.

3.2. *Thermogravimetric analysis*

Thermogravimetric analysis has been performed on the solid complexes in order to verify the number of water molecules in these complexes (table 1). The TG plot of $[Cu_2(OH)_2(H_2O)_2(py\text{-}triaz)(bz\text{-}leu)_2]\cdot 4H_2O$ exhibited two resolved and un-overlapped decomposition steps. The first step occurred at a temperature range 80–100°C, corresponding to 7.1% weight loss from loss of four solvated water molecules. In the second decomposition step (160–180°C), the molecule lost two coordinated water molecules and two OH groups, with a total weight loss of 13.98%.



Scheme 2. The proposed structures of the copper complexes.

Table 3. Crystal parameters and X-ray diffraction data for $[Cu(imi)_2(Ac\text{-}phgly)_2] \cdot H_2O$ complex.

Complex	$[Cu(imi)_2(Ac\text{-}phgly)_2] \cdot H_2O$
Formula	$C_{26}H_{32}CuN_6O_8$
M	620.116
Space group	$P\bar{1}$
Cell parameters (Å, °)	
a	8.4261(3)
b	9.4733(3)
c	10.1498(3)
α	116.205(2)
β	93.223(2)
γ	96.2195(12)
Cell volume (Å^3)	717.70(4)
Z	1
D ($g\,cm^{-1}$)	1.435
No. of reflections	30
Temperature (K)	298
Diffractometer	maXus (Bruker Nonius, Delft & MacScience, Japan)
μ (cm^{-1})	0.82
Radiation, λ (Å)	Mo-Kα, 0.71073
θ range (°)	3–33
h, k, l range	0, 12; ±14; ±15
No. of reflections measured	5180
No. of reflections used in the refinement [$I > 3.00\sigma(I)$]	2948
No. of refined parameters	187
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.039
$R' = [\Sigma\|w\Delta F^2/\Sigma w F_o^2]^{1/2}$	0.059

The TG plot of [Cu(imi)$_2$(Ac-phgly)$_2$]$\cdot$H$_2$O displayed an initial slow weight loss of 2.89% in the range 50–150°C, which is in accord with the loss of one water of hydration (figure 4).

3.3. *EPR measurements*

The X-band EPR spectra of the polycrystalline samples of the binuclear complexes [Cu$_2$(qox)(bz-leu)$_4$], [Cu$_2$(OH)$_2$(H$_2$O)$_2$(py-triaz)(bz-leu)$_2$] and the previously reported [Cu$_2$(OH)(H$_2$O)(bpy)$_2$(ambz-gly)](NO$_3$)$_2$, ambz-gly = 4-aminobenzoyl glycinate [18], were carried out at room temperature. These spectra are single broad signals due to $\Delta Ms = \pm 1$ at $g = 2.08$. $\Delta Ms = \pm 2$ signal (half-field signal) is observed, characteristic of a magnetic triplet [19]. This type of signal is characteristic for binuclear copper(II) complexes in which there is a magnetic interaction between two paramagnetic metal centers. The absence of hyperfine structures from the spectral curves points to the presence of dipolar interactions. Similar spectra have been observed for imidazolate-bridged and other dicopper(II) complexes and have been interpreted in terms of dipolar coupling of Cu(II) ions [19, 20–23].

Figure 1 shows the EPR spectrum of the polycrystalline sample of [Cu$_2$(qox)(bz-leu)$_4$]. The Cu(II) ions are in an axially symmetric coordination as inferred from the g values ($g_1 = 2.075$, $g_2 = 2.075$, $g_3 = 2.140$). Moreover, the g values indicate a $d_{x^2-y^2}$ ground state for the d^9 Cu(II) (SCu = 1/2) having one unpaired electron in a $d_{x^2-y^2}$ orbital. Such a spectrum can be observed for copper(II) in axial symmetry with all the principal axes aligned parallel and would be consistent with an elongated tetragonal octahedron [24].

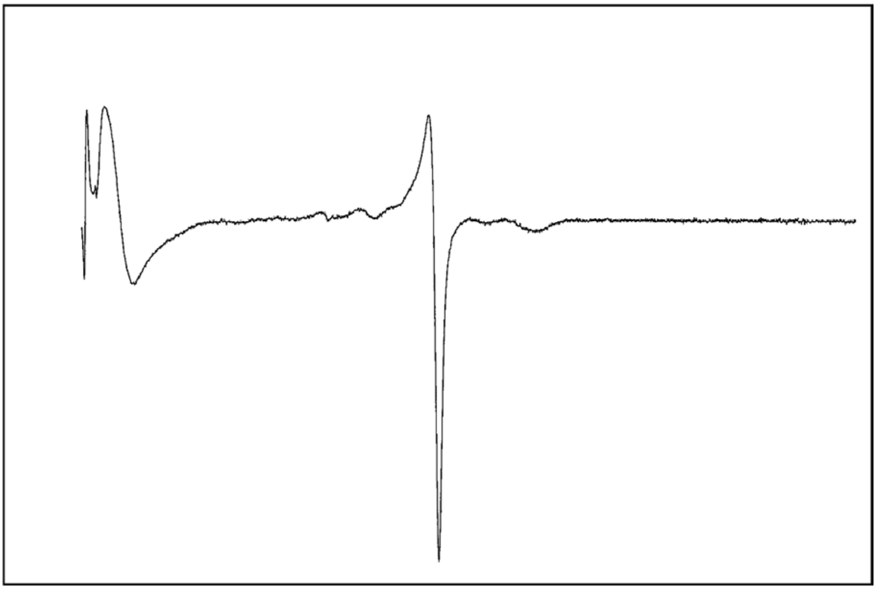


Figure 1. X-band EPR spectrum of the polycrystalline [Cu$_2$(quinox)$_2$(bz-leu)$_4$].

The EPR spectrum of $[Cu_2(OH)_2(H_2O)_2(py\text{-}triaz)(bz\text{-}leu)_2]$ is also consistent with an axial type spectrum with $g_\perp > 2.04$ (figure 2).

The EPR spectrum of $[Cu_2(OH)(H_2O)(bpy)_2(ambz\text{-}gly)](NO_3)_2$ complex showed a lower $g_\perp > 2.03$ (figure 3). This spectrum can be observed for a copper(II) in axial symmetry with the principal axes aligned parallel and would be consistent with compressed trigonal bipyramidal stereochemistry. Singlet–triplet ($\Delta Ms = \pm 2$) transition is expected for dimeric structures containing magnetically coupled copper(II) centers [25].

3.4. *Crystal structure of [Cu(imi)$_2$(Ac-phgly)$_2$] • H$_2$O*

The crystal structure of *bis*-(*N*-(acetyl)phenylglycinato)-*bis*-(imidazole)copper(II) was determined by X-ray analysis. The crystallographic data are presented in table 3. Projection and packing of $[Cu(imi)_2(Ac\text{-}phgly)_2] \cdot H_2O$ are illustrated in figures 4 and 5. Selected bond lengths and angles of the complex are given in table 4. The structure of the complex consists of monomeric units, in which the copper atom exists in a square planar geometry with a CuN_2O_2 chromophore, with two centrosymmetrically related carboxyl oxygens and imidazole nitrogen atoms. Such a structure is similar to those previously reported for copper(II) complexes, with square planar geometry and a *trans*-CuN_2O_2 chromophore. For example, the structures of $[Cu(bzglyO)_2(imi)_2]$ [26], $[Cu(ac\text{-}\alpha\text{-}alaO)_2(meim)_2] \cdot 2H_2O$ [27] and $[Cu(Z\text{-}\alpha\text{-}alaO)_2(meim)_2] \cdot C_2H_2OH$ [28]. For these complexes, the global view of the structural and spectroscopic results [29] excluded involvement of a second carboxylate oxygen in the metal ion coordination for the same reasons as those proposed for the binary compounds $[Cu(acglyO)_2(H_2O)_2] \cdot 2H_2O$ [30] and $[Cu(ac\text{-}\beta\text{-}alaO)_2(H_2O)_2]$ [31]. These findings were based only on the shortness of

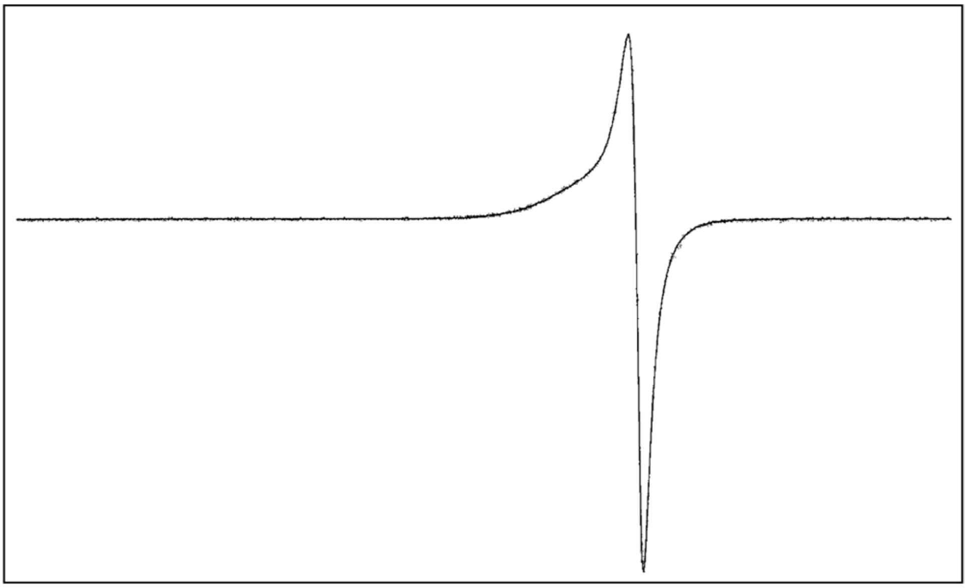


Figure 2. X-band EPR spectrum of the polycrystalline $[Cu_2(OH)_2(H_2O)_2(2\text{-}py\text{-}triazin)(bz\text{-}leu)_2] \cdot 4H_2O$ at room temperature.

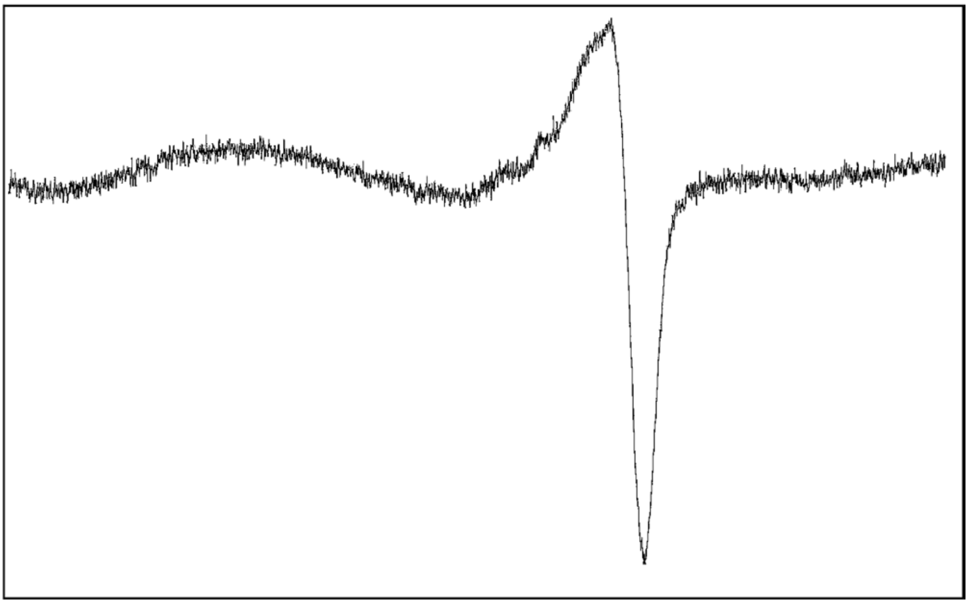


Figure 3. X-band EPR spectrum of the polycrystalline $[Cu_2(OH)(H_2O)(2,2'\text{-bipy})_2(\text{Am-bz-gly})](NO_3)_2 \cdot 4H_2O$ at room temperature.

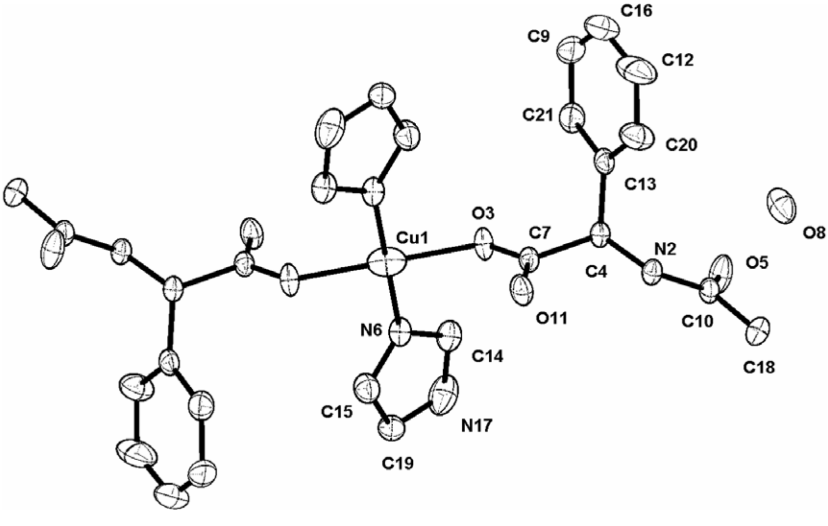


Figure 4. Projection of $[Cu(imi)_2(\text{Ac-phgly})_2] \cdot H_2O$.

the Cu···O(2) distance (2.614(3) and 2.580(2) Å for the above two compounds, respectively) where the second carboxylate oxygens are not sufficient to assign a tetragonal geometry. It seems more correct to consider those distances as non-bonding interactions, since the angle between the Cu–O(2) vector and the normal to the O(1) O(4) $O(1^-)$ $O(4^-)$ plane of 36.4° [32] and 33.8° [32], respectively, prevents overlap of the metal-ligand orbitals. For the structure of $[Cu(acphgly)_2(imi)_2(H_2O)_2]$ [33]

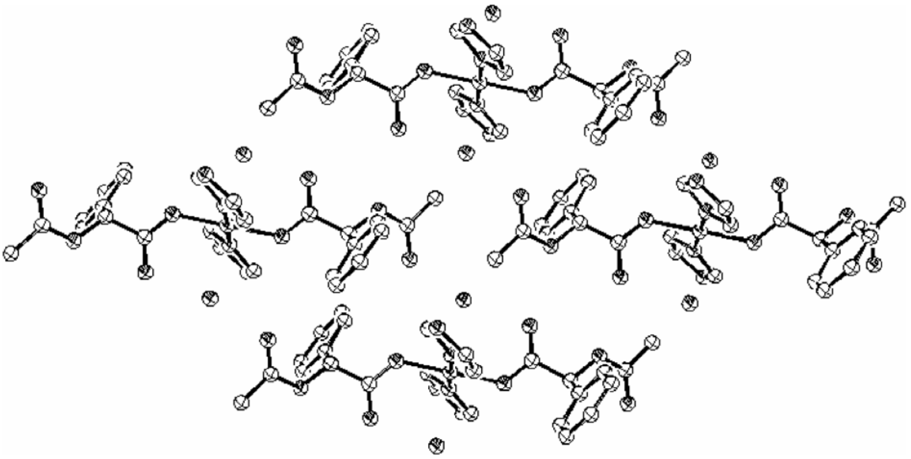


Figure 5. Packing of $[Cu(imi)_2(Ac\text{-}phgly)_2]\cdot H_2O$ complex.

Table 4. Selected bond lengths(Å) and bond angles(°) for $[Cu(imi)_2(Ac\text{-}phglry)_2]\cdot H_2O$.

Cu1–O3	1.952(2)	O3–C7	1.263(4)
Cu1–N6	1.978(3)	O3–O11	2.239(4)
C4–C7	1.543(5)	N2–C4	1.446(4)
C7–O11	1.233(5)	N2–C10	1.340(4)
N2–O11	2.714(4)	C7–C13	2.490(5)
N2–C13	2.476(5)	N6–C14	1.375(5)
N2–C18	2.411(5)	N6–C15	1.324(6)
C4–C7	1.543(5)	O3–C4	2.341(4)
C4–O5	2.742(4)	O3–N6	2.748(4)
O3–Cu1–N6	88.70(13)	N6–O3–C7	124.5(3)
Cu1–O3–C4	165.8(2)	N6–O3–O11	108.6(2)
Cu1–O3–N6	46.04(9)	C7–O3–O11	25.9(2)
Cu1–O3–C7	128.3(3)	N2–C4–O3	137.6(3)
Cu1–O3–O11	102.42(14)	N2–C4–O5	54.6(2)
Cu1–N6–O3	45.26(9)	N2–C4–C7	110.3(3)
Cu1–N6–C14	128.5(3)	N2–C4–C10	27.9(2)
Cu1–N6–C15	125.1(3)	N2–C4–O11	85.7(2)
Cu1–N6–N17	163.4(2)	Cu1–N6–C19	159.4(2)
C4–O3–C7	37.5(2)	C4–N2–C7	36.1(2)
C4–N2–O11	62.2(2)	C4–N2–C10	121.7(3)

Cu–OH_2 distances of 2.912(5) Å and the angle with the normal to the coordination plane of 8.6(2)° suggest $CuN_2O_2O'_2$ chromophore. The structure was found to be similar to those found for similar ternary complexes with amines of low basicity, such as pyridines.

In the crystal, the molecules are connected by H-bonds involving the water molecules, the carboxylate oxygen atoms and peptide nitrogen of the *N*-(acetyl)phenylglycinate, figure 5. Two types of hydrogen bonds are observed. The first type is intramolecular hydrogen bonds resulting from interaction between the lattice water molecules and the coordinated carboxylate oxygen atoms ($O3\cdots H8B^{iv} = 1.86(4)$ Å ($iv = x-1,\ 1+y,\ z$) $O3\cdots H8B^{v} = 2.00(4)$ ($v = 1-x,\ 1-y,\ -z$). Also, the uncoordinated carboxylate oxygen forms a hydrogen bond with an adjacent peptidic nitrogen ($O11\cdots H_2^{vii} = 2.65(4)$ Å (vii $= -x,\ 2-y,\ 1-z$). From the packing of the unit cell, it can be postulated that the intermolecular hydrogen bond gives rise to a zigzag chain structure (figure 5).

Supplementary data

Supplementary crystallographic data are available from the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK on request, deposition number: CCDC 614466.

References

[1] K.D. Karlin, Z. Tyeklar. *Bioinorganic Chemistry of Copper*, Chapman & Hall, New York (1993).
[2] R.H. Holm, P. Kennepohl, E.I. Solomon. *Chem. Rev.*, **96**, 2239 (1996).
[3] J.P. Klinman. *Chem. Rev.*, **96**, 2541 (1996).
[4] R. Than, A.A. Feldmann, B. Krebs. *Coord. Chem. Rev.*, **182**, 211 (1999).
[5] J. Reedijk, E. Bouwman. *Bioinorganic Catalysis*, 2nd Edn, Marcel Dekker, New York (1999).
[6] M.R. Malachowski, J. Carden, M.G. Davidson, W.L. Driessen, J. Reedjik. *Inorg. Chim. Acta*, **257**, 59 (1997).
[7] C. Chailuecha, S. Youngme, C. Pakawatchai, N. Chaichit, G. Van Albada, J. Reedijk. *Inorg. Chim. Acta*, **359**, 4168 (2006).
[8] K.A. Magnus, H. Ton-That, J.E. Carpenter. *Chem. Rev.*, **94**, 727 (1994).
[9] J. Ling, L.P. Nestor, R.S. Czernuszewicz. *J. Am. Chem. Soc.*, **116**, 7682 (1994).
[10] A.G. Sykes. *Advances in Inorganic and Bio-organic Mechanisms*, Academic Press, London (1983).
[11] S. Mackay, C.J. Gilmore, C. Edwards, N. Stewart, K. Shankland. *maXus Computer Program for the Solution and Refinement of Crystal Structures*. Bruker Nonius, The Netherlands, MacScience, Japan & The University of Glasgow (1999).
[12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli. *J. Appl. Cryst.*, **27**, 435 (1994).
[13] C.K. Johnson. *ORTEP–II. A Fortran Thermal–Ellipsoid Plot Program. Report ORNL-5138*. Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA (1976).
[14] D. Waasmaier, A. Kirfel. *Acta Cryst.*, **A51**, 416 (1995).
[15] R.H. Blessing. *Acta Cryst.*, **A51**, 33 (1995).
[16] J.R. Ferraro. *Low-frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York (1971).
[17] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley, New York (1986).
[18] P. Sgarabotto, F. Bisceglie, G. Pelosi, L. Abdel-Rahman. *Polyhedron*, **18**, 2505 (1999).
[19] T.D. Smith, J.L. Pilbrow. *Coord. Chem. Rev.*, **13**, 173 (1974).
[20] R.N. Patel, S. Kumar, K.B. Pandeya. *Spectrochim. Acta Part A*, **56**, 791 (2000).
[21] R.N. Patel, S. Kumar, K.B. Pandeya. *J. Inorg. Biochem.*, **89**, 61 (2002).
[22] R.N. Patel, S. Kumar, K.B. Pandeya, P.V. Khadhikar. *Spectrochim. Acta Part A*, **58**, 2961 (2002).
[23] R.N. Patel. *Spectrochim. Acta Part A*, **59**, 713 (2003).
[24] R.N. Patel, N. Singh, K.K. Shukla, U.K. Chauhan. *Spectrochim. Acta Part A*, **61**, 287 (2005).
[25] G. Facchin, M.H. Torre, E. Kremer, E.J. Baran, A. Mombru, H. Pardo, M.P. Araujo, A.A. Batista. *J. Inorg. Chim. Acta*, **355**, 408 (2003).
[26] L. Antolini, L.P. Battaglia, A.B. Corradi, G. Marcotrigiano, L. Menabue, G.C. Pellacani, M. Saladini. *Inorg. Chem.*, **21**, 1391 (1982).
[27] L.P. Battaglia, A.B. Corradi, L. Menabue, G.C. Pellacani, P. Prampolini, M. Saladini. *J. Chem. Soc. Dalton Trans.*, 781 (1982).
[28] L. Antolini, L. Menabue, M. Saladini, M. Sola, L.P. Bttaglia, A.B. Corradi. *Inorg. Chem. Acta*, **93**, 61 (1984).
[29] L. Antolini, L.P. Battaglia, A.B. Corradi, G. Marcotrigiano, L. Menabue, G.C. Pellacani. *J. Am. Chem. Soc.*, **107**, 1369 (1985).

[30] G. Marcotrigiano, G.C. Pellacani, L.P. Battaglia, A.B. Corradi. *Cryst. Struct. Commun.*, **5**, 923 (1976).
[31] L.P. Battaglia, A.B. Corradi, G. Marcotrigiano, L. Menabue, G.C. Pellacani. *Inorg. Chem.*, **20**, 1075 (1981).
[32] M.R. Udupa, B. Krebs. *Inorg. Chim. Acta*, **31**, 251 (1978).
[33] A. Corradi Bonamartini, S. Bruni, F. Cariati, L.P. Battaglia, G. Pelosi. *Inorg. Chim. Acta*, **205**, 99 (1993).