

# SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF N-ACETYL-DL-PHENYL-GLYCINATO COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II). CRYSTAL STRUCTURES OF BIS(N-ACETYL-DL-PHENYL-GLYCINATO)DIAQUOBIS-(N-METHYLIMIDAZOLE)COBALT(II), BIS(N-ACETYL-DL-PHENYLGLYCINATO)DIAQUOBIS (IMIDAZOLE)COBALT(II) AND NICKEL(II)

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**Abstract**—A series of complexes of N-acetyl-DL-phenylglycine and Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> containing heterocyclic bases as imidazoles, phen, bipy and terpy were prepared and characterized by conventional methods, IR spectra and, for  $[Co(OH_2)_2(mini)_2(Ac-phgly)_2]$  (1),  $[Co(OH_2)_2(imi)_2(Ac-phgly)_2]$  (2) and  $[Ni(OH_2)_2(imi)_2(Ac-phgly)_2$  (3), by X-ray crystal structure. The structure of these complexes consists of discrete  $[M(OH_2)_2(mini)_mi)_2(Ac-phgly)_2]$  units in which the metal shows nearly ideal centrosymmetrical *trans*-octahedral geometry bonding two imidazole nitrogens, two carboxylic oxygens and two water molecules. In all cases the amino acid behaves as monodentate via carboxylic oxygen, the second carboxylic oxygen; the NH and CO peptide groups are involved in hydrogen bonds which are responsible for the packing in the crystal.

There is a great interest in the structural and spectroscopic properties of metal(II) complexes with Nprotected amino acids, where the protecting groups can be acetyl, benzoyl or tosyl, deriving from the

➡Deceased.

fact that they may supply information about bonding characteristic of protein-like donor molecules toward metal ions. N-protected amino acids also show relevance for their involvement in some biological processes. From this point of view N-acetyl derivatives, present in some natural proteins and peptides, are the most important, being considered as the starting units in the biosynthesis of some

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peptide chains.<sup>1</sup> The coordination properties of Nacetyl-DL-phenyl-glycine (hereafter Ac-phgly) were previously studied in  $[Cu(OH_2)_2(imi)_2(Ac$  $phgyl)_2]^2$  where it was found the presence of monomeric copper complexes having distorted octahedral geometry and the amino acid behaves as monodentate via carboxylic oxygen. With the aim of elucidating these properties in order to understand more complicated biological systems showing the role and the coordination mode of the amino acid, a systematic study on transition metal ternary complexes with imidazoles was undertaken.

# **EXPERIMENTAL**

#### Preparation of cobalt(II) and nickel(II) complexes

The  $[Co(OH_2)_2(mini)_2(Ac-phgly)_2]$  (1),  $[Co(OH_2)_2(ini)_2(Ac-phgly)_2]$  (2) and  $[Ni(OH_2)_2(ini)_2(Ac-phgly)_2]$  (3) were prepared by mixing cobalt(II) or nickel(II) acetate (2 mmol in 20 cm<sup>3</sup>) and N-acetyl-DL-phenylglycine (2 mmol in 20 cm<sup>3</sup>) in a methanol-water 1:1 mixture, followed by the addition of a methanolic solution of imidazole or N-methylimidazole (4 mmol in 10 cm<sup>3</sup>). The mixture was refluxed for 2 h, then these solutions were covered : after nearly 3 weeks a crystalline material was deposited.

The complex  $[Ni(OH_2)_2(mimi)_2(Ac-phgly)_2]$  (4) was prepared by reacting the binary Ni(Acphgly)\_2 · 4H<sub>2</sub>O complex in methanol (0.1 mmol in 20 cm<sup>3</sup>) with N-methylimidazole (0.2 mmol in 20 cm<sup>3</sup>) : after 3–4 weeks the complex precipitated.

#### Preparation of copper(II) complexes

The class of complexes was prepared by direct reaction among copper perchlorate hexahydrate (1 mmol), N-acetyl-DL-phenylglycine (1 mmol) and 2,2'-bipy, 1,10-phen or 2,2',2"-terpyridine (L, 1 mmol, molar ratios 1:1:1). The reagents were dissolved in 50 cm<sup>3</sup> of a methanol-water 1:1 mixture, the resulting solutions were slowly evaporated: after 2 weeks blue complexes with general formula  $[Cu(L)(Ac-phgly)](ClO_4) \cdot H_2O$  (compounds 5, 6, 7) were obtained. Table 1 shows the results of the elemental analyses, melting points and colors of the products.

#### Instrumental equipment

The elemental analyses (C, H and N contents) were performed on a Carlo Erba CHNSO EA1108 Elemental Analyzer. The IR spectra were collected in the 4000–400 cm<sup>-1</sup> region on a Nicolet 5PC FT-IR Spectrometer using KBr disks. Melting points were obtained with a Gallenkamp MFB-595 Apparatus in open capillaries.

#### *Crystallography*

The crystals of 1, 2 and 3 mounted on a glass fiber, were examined by X-ray diffraction using automated four-circles computer controlled diffractometers. The crystal data and relevant details concerning data collection and refinements are quoted in Table 2; compounds 2 and 3 resulted isostructural. The intensities  $I_{\rm hkl}$  were determined

 Table 1. Elemental analyses, formula weights and melting points of (M(II)-(imi, mimi, bipy, phen, terpy)-N-Acetyl-DL-phenylglycine ternary complexes

Complex	FW	C(%)	H(%)	N(%)	MP(°C)
[CO(OH <sub>2</sub> ) <sub>2</sub> (mimi) <sub>2</sub> (Ac-phgly) <sub>2</sub> ]	643.64	52.2	5.6	13.0	149
Rose crystals		(51.7)	(4.2)	(13.0)	
$[Co(OH_2)_2(imi)_2(Ac-phgly)_2]$	615.55	50.7	5.2	13.6	147
Violet crystals		(49.8)	(4.4)	(13.5)	
$[Ni(imi)_2(Ac-phgly)_2] \cdot 2H_2O$	615.33	50.7	5.2	13.6	185
Light-blue crystals		(49.7)	(4.4)	(13.6)	
$[Ni(mimi)_2(Ac-phgly)_2] \cdot 2H_2O$	643.42	52.2	5.6	13.1	177
Light-blue powder		(51.6)	(4.3)	(12.9)	
$[Cu(bipy)(Ac-phgly)](ClO_4) \cdot 2H_2O$	574.42	43.8	4.0	7.7	195
Blue powder		(43.6)	(3.7)	(7.4)	
$[Cu(phen)(Ac-phgly)](ClO_4 \cdot 2H_2O)$	572.46	46.1	4.0	7.3	210
Greenish-blue crystals		(46.5)	(3.6)	(7.4)	
$[Cu(terpy)(Ac-phgly)](ClO_4) \cdot 2H_2O$	625.50	48.0	4.2	8.9	252
Greenish-blue crystals		(48.0)	(3.9)	(8.9)	

Compound	(1)	(2)	(3)
Formula	$C_{28}H_{16}CoN_6O_8$	C <sub>26</sub> H <sub>32</sub> CoN <sub>6</sub> O <sub>8</sub>	C <sub>26</sub> H <sub>32</sub> NiN <sub>6</sub> O <sub>8</sub>
Μ	643.56	615.51	615.28
Space group	P1	$P2_1/n$	$P2_1/n$
a(Å)	10.365(8)	10.490(3)	9.542(2)
$b(\mathbf{\hat{A}})$	9.482(3)	15.727(3)	15.593(3)
$c(\mathbf{A})$	9.580(5)	9.564(2)	10.447(3)
$\alpha(\cdot)$	110.42(3)	90	90
$\beta()$	117.97(5)	116.00(10)	116.00(10)
$\gamma(2)$	77.75(4)	90	90
$V(Å^3)$	777.9(8)	1418(1)	1397(1)
Ζ	1	2	2
$D_{\varsigma}(\text{gcm}^{-3})$	1.37	1.44	1.46
Reflections for lattice parameters			
number	25	30	30
$\theta$ range	9.6-15.6	12.0 - 18.7	16.7-36.2
F(000)	337	642	644
Temperature(K)	294	294	294
Diffractometer	Philips PW1100	Siemens AED	Siemens AED
Crystal size(mm)	$0.33 \times 0.45 \times 0.51$	0.38  imes 0.58  imes 0.86	$0.10 \times 0.23 \times 0.33$
$\mu(\mathrm{cm}^{-1})$	6.08	6.6	15.1
Radiation, $\lambda(\text{\AA})$	Mo- $K_{\alpha}$ 0.7107	<b>Mo-K</b> <sub><math>\alpha</math></sub> 0.7107	Cu-K <sub>x</sub> 1.5418
Scan speed ( $^{\circ}$ min <sup>-1</sup> )	2.4-7.2	3.0-12.0	3.0-12.0
Scan width(°)	$1.4 + 0.35 \tan\theta$	$1.2 \pm 0.35 \tan\theta$	$1.3 \pm 0.35 \tan\theta$
$\theta$ range(°)	3–25	3-30	3-65
h.k,l range	$\pm 14; \pm 13; 0.13$	$\pm 14; 21; 0.13$	$\pm 13; 0,20; 0,14$
Standard reflection	-2 - 55	-338	-174
Max. intensity variation(%)	3.5	4.5	4.6
Scan mode	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
No. of reflections measured	2915	3284	2629
No. of reflections used in the			
refinement $[I > 2\sigma(I)]$	1887	3116	1936
No. of refined parameters	268	251	251
$R = \Sigma  \Delta F  / \Sigma  F_0 $	0.0259	0.0397	0.0325
$R' = [\Sigma w(\Delta F^2) / \Sigma w F_0^2]^{1/2}$	0.0291	0.0499	0.0375
$k.g$ in $w = k[\sigma^2(F_0) + gF_0^2]^{-1}$	0.29, $2.4 \times 10^{-3}$	$0.5, 4.6 \times 10^{-3}$	$1.08, 8.4 \times 10^{-4}$
Max., min. height in final $\Delta F$ map (eÅ <sup>-3</sup> )	-0.18, 0.27	-0.74, 0.77	-0.24, 0.52

Table 2. Experimental data for the crystallographic analyses

by analysing the reflection profiles and were corrected for Lorentz and polarization effects. The structures were solved by Patterson methods and refined by full-matrix least-squares with anisotropic thermal parameters. Hydrogens, located in a  $\Delta F$ map, were isotropically introduced in the last cycle of the refinements. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.<sup>3</sup> All the calculations were performed on a Encore E91 computer using SHELX76,<sup>4</sup> ORTEP<sup>5</sup> and PARST<sup>6</sup> programs.

#### **RESULTS AND DISCUSSION**

# Infrared spectra

The most significant frequencies in the IR spectra of the cobalt and nickel ternary complexes (compounds 1, 2, 3, 4) are shown in Table 3, while those of copper are quoted in Table 4 (compounds 5, 6, 7). These spectra are characterized by a broad band in the range 3464-3402 cm<sup>-1</sup> which can be ascribed to the stretching vibrations of water molecules. The distinct very strong band in the region 3349–3308 cm<sup>-1</sup> can be referred to the NH stretching of the amino acid. The imidazole NH stretching present in compounds 2 and 3 at 3204 and  $3203 \text{ cm}^{-1}$  is lacking in complexes 1 and 4. The v(CO) amide stretching bands fall in the range 1659–1585 cm<sup>-1</sup> for all complexes. The presence of a very strong band in the region 1604–1585  $cm^{-1}$ , which is typical of coordinated carboxylate group, confirms the coordination of the amino acid through the carboxylic oxygen. However, for all complexes the bands in the region 1387-1316 cm<sup>-1</sup>

Tuble 5. Initiated spectra of Co(II), 14(II) init, initia and 14 active DE pitchylg	ycine				
ternary complexes					

Assignment	Complex 1	Complex 2	Complex 3	Complex 4
$v_{as}(OH_2)$	3470sh	3495sh	3503sh	
v <sub>s</sub> (OH <sub>2</sub> )	3402sh	3422sh	3417m	
(NH), amide	3318vs	3308vs	3313vs	3321vs
v(NH), imidazol		3204sh	3203sh	
v(CO), amide	1658vs	1631m	1631m	1659vs
$v_{as}(CO_2)$	1597vs	1597vs	1599vs	1604vs
$v_{s}(CO_{2})$	1386vs	1384vs	1384vs	1387vs

Complex 1: Co(OH<sub>2</sub>)<sub>2</sub>(mimi)<sub>2</sub>(Ac-phgly)<sub>2</sub>].

Complex 2:  $[Co(OH_2)_2(imi)_2(Ac-phgly)_2].$ 

Complex  $3 : [Ni(OH_2)_2(imi)_2(Ac-phgly)_2].$ 

Complex 4: [Ni(OH<sub>2</sub>)<sub>2</sub>(mimi)<sub>2</sub>(Ac-phgly)<sub>2</sub>].

Table 4. Infrared spectra of Cu(II)-2,2'-bipy, 1,10-phen,2,2',2"-terpy and N-acetyl-DL-phenylglycine ternary<br/>complexes

Assignment	Complex 5	Complex 6	Complex 7
$v_{as}(OH_2)$		3530sh	3522sh
$v_{s}(OH_{2})$	3402b		3464sh
v(NH), amide		3349s	3348vs
v(CO), amide	1617vs	1618vs	1624vs
$v_{av}(CO_2)$	1603sh	1585sh	1603s
$v_{\rm s}({\rm CO}_2)$	1316m	1344s	1339s

Complex 5:  $[Cu(OH_2)_2(bipy)(Ac-phgly)](ClO_4)$ . Complex 6:  $[Co(OH_2)_2(phen)(Ac-phgly)](ClO_4)$ . Complex 7:  $[Cu(OH_2)(terpy)(Ac-phgly)](ClO_4) \cdot H_2O$ .

can be ascribed to the symmetric stretching vibration of the coordinated carboxylate. Copper ternary complexes are characterized by further bands in the range 1109-1092 cm<sup>-1</sup> attributed to the stretching of the perchlorate group.

# Crystal structures

The structures of the complexes  $[Co(OH_2)_2 (mimi)_2(Ac-phgly)_2]$  (1),  $[CO(OH_2)_2(imi)_2(Ac-phgly)_2]$  (2) and  $[Ni(OH_2)_2(imi)_2(Ac-phgly)_2]$  (3) consist of discrete neutral molecules in which the metal, located on a symmetry center, exhibits nearly regular *trans*-octahedral geometry bonding two heterocyclic molecules, two water and Ac-phgly ions acting as monodentate *via* carboxylic oxygens (Figs

1 and 2). Table 5 shows selected bond distances and angles for the structures; as the trans angles are all 180° for symmetry requirements and the cis ones are in the range  $87.1(1)-91.1(1)^{\circ}$  for 1, 88.5(1)-91.8(1)° for 2 and 88.5(1)-91.9(1)° for 3, it is evident that only bond distances around the metal are responsible for some small deformations in the polyhedra. These values show in all cases a similar trend, the carboxylate oxygen is more strongly bonded if compared to the other neutral ligands, the bonds of water molecules are the longer and the values of imidazole are intermediate. These values compare well with those previously found in the literature, e.g. for cobalt complexes, in  $[Co(imi)_4]$  $(OH_2)_2^{2+,7}$  CO-N = 2.125(2), 2.164(2) Å; Co-Ow = 2.140(2) Å; in  $[Co(CO_3)(OH_2)_2(imi)_2, ^8 Co N = 2.112(7) \text{ Å}; Co-O(COO^{-}) = 2.143(5) \text{ Å}; Co-$ Ow = 2.166(6) Å. Similar examples can be found for the nickel complex : in [Ni(imi)<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>,<sup>9</sup> Ni- $N = 2.094(2), 2.113(2) \text{ Å}; \text{ in } [Ni(gly)_2(imi)_2]^{10}$ (gly = glycinato), Ni-N(imi) = 2.060(4), 2.086(3)Å, Ni–O(COO<sup>-</sup>) = 2.071(3), 2.108(3) Å. As found in the structure of the  $[Cu(OH_2)_2(imi)_2(Ac-phgly)_2]^2$ complex also in all these compounds the amino acid acts as simple carboxylate, the conditions to obtain the NH deprotonation and formation of a fiveterms chelate ring not being reached. Bond distances and angles of Ac-phgly are very similar in these compounds and in the copper complex. The carboxylic group, including the  $\alpha$ -carbon, the peptide group, the phenyl and imidazole rings are planar within the experimental errors. The conformation of the amino acid is similar in all cases. Table 6 reports for these structures and the copper complex the torsion angles around the C(2)-C(3)



Fig. 1. Arbitrary view of the complex molecule 1.



Fig. 2. Arbitrary view of the complex molecule 2.

Compound	1 M = Co	2 M = Co	3 M – Ni
	M = C0		
MO(31)	2.075(3)	2.055(3)	2.035(3)
M—Ow	2.145(2)	2.186(3)	2.132(3)
MN(4)	2.131(2)	2.130(2)	2.076(2)
O(11)—C(11)	1.234(3)	1.238(3)	1.235(3)
O(31)—C(3)	1.253(3)	1.255(3)	1.252(3)
O(32)—C(3)	1.245(3)	1.248(3)	1.244(3)
N(1)—C(2)	1.444(4)	1.454(3)	1.449(3)
N(1)—C(11)	1.327(5)	1.335(3)	1.336(4)
N(4)—C(5)	1.318(3)	1.324(3)	1.325(4)
N(4)C(8)	1.368(5)	1.368(3)	1.368(4)
N(6)—C(5)	1.341(4)	1.348(3)	1.337(4)
N(6)—C(6)	1.466(6)		
N(6)—C(7)	1.358(5)	1.360(4)	1.360(4)
C(2)—C(3)	1.537(4)	1.545(3)	1.550(3)
C(2)C(21)	1.527(4)	1.522(2)	1.520(2)
C(7)—C(8)	1.353(5)	1.359(3)	1.335(4)
C(11)—C(12)	1.498(5)	1.498(4)	1.494(4)
C(21)C(22)	1.379(4)	1.392(3)	1.393(4)
O(31)—M—Ow	89.1(1)	91.3(1)	90.8(1)
O(31) - M - N(4)	91.1(1)	88.5(1)	88.5(1)
N(4)—M—Ow	87.1(1)	91.8(1)	91.9(1)
M - O(31) - C(3)	131.3(2)	133.0(2)	132.2(2)
C(2) - N(1) - C(11)	122.6(3)	121.6(2)	121.9(2)
M - N(4) - C(5)	126.1(2)	126.5(1)	126.7(2)
M - N(4) - C(8)	128.5(2)	127.9(1)	128.6(2)
C(5) - N(4) - C(8)	105.0(2)	105.6(2)	104.7(3)
C(5) - N(6) - C(6)	126.0(3)		
C(5)-N(6)-C(7)	106.7(3)	107.5(2)	106.7(3)
C(6) - N(6) - C(7)	127.3(3)		
N(1) - C(2) - C(3)	111.5(2)	111.8(2)	112.1(2)
N(1) - C(2) - C(21)	113.7(2)	114.1(2)	114.4(1)
C(3) - C(2) - C(21)	108.4(2)	108.9(1)	108.9(2)
O(31)-C(3)-O(32)	127.3(3)	127.4(2)	127.7(2)
O(31) - C(3) - C(2)	113.9(2)	112.7(2)	113.0(2)
O(32) - C(3) - C(2)	118.8(2)	119.9(2)	119.3(2)
N(4) - C(5) - N(6)	111.9(2)	110.9(2)	111.5(2)
N(6)—C(7)—C(8)	106.7(3)	106.2(2)	106.9(3)
N(4)—C(8)—C(7)	109.7(3)	109.8(2)	110.1(3)
O(11) - C(11) - N(1)	121.2(2)	122.3(2)	122.1(3)
O(11) - C(11) - C(12)	121.7(3)	120.8(2)	120.8(2)
N(1) - C(11) - C(12)	117.1(3)	117.0(2)	117.1(2)

Table 5. Selected bond distances and angles with e.s.d.s in parentheses

Complex	N(1)—C(2)—C(3)—O(31) C(3)—C(2)—N(1)—C(11)	$ph \wedge pg$	$ph \wedge carb$	pg∧carb
[Co(OH <sub>2</sub> ) <sub>2</sub> (mimi) <sub>2</sub> (Ac-phgly) <sub>2</sub> ]	- 159.4(2)	73.2(1)	74.2(2)	33.0(2)
	143.2(2)			
$[Co(OH_2)_2(imi)_2(Ac-phgly)_2]$	-163.1(2)	70.5(1)	70.4(2)	40.0(1)
	135.7(2)			
[Ni(OH <sub>2</sub> ) <sub>2</sub> (imi) <sub>2</sub> (Ac-phgly) <sub>2</sub> ]	-162.6(2)	71.3(1)	70.6(2)	39.2(2)
	136.4(2)			
[Cu(OH <sub>2</sub> ) <sub>2</sub> (imi) <sub>2</sub> (Ac-phgly) <sub>2</sub> ]	-158.9(4)	71.0(2)	73.3(2)	37.6(1)
	138.6(2)			

Table 6. Significant torsion and dihedral angles (°) in the N-Acetyl-DL-phenylglycine ligand

Abbreviations: ph = phenyl ring, pg = peptide group, carb = carboxylic group.

Compound 1			
N(1)—H(1)	$N(1) \cdots O(32^a)$	$H(1) \cdots O(32^a)$	$N(1)$ — $H(1) \cdots O(32^{a})$
0.77(2)	2.993(3)	2.28(2)	154(3)
Ow—H(2w)	$Ow \cdots O(32^b)$	$H(2w) \cdots O(32^b)$	$Ow - H(2w) \cdots O(32^{h})$
0.83(4)	2.752(4)	2.00(4)	150(3)
Ow—H(1w)	$\mathbf{Ow}\cdots\mathbf{O}(11^c)$	$H(1w) \cdots O(11^c)$	$Ow - H(1w) \cdots O(11^{\circ})$
0.79(4)	2.750(3)	1.97(4)	169(3)
Compound 2			
N(1) - H(1)	$N(1) \cdots O(32^a)$	$H(1) \cdots O(32^a)$	$N(1) - H(1) \cdots O(32^{a})$
0.71(2)	3.034(5)	2.37(2)	157(3)
Ow-H(2w)	$Ow \cdots O(32^b)$	$H(2w) \cdots O(32^{h})$	$Ow - H(2w) \cdots O(32^{b})$
0.74(4)	2.792(4)	2.08(4)	168(3)
Ow—H(1w)	$\mathbf{Ow}\cdots\mathbf{O}(11^f)$	$H(1w) \cdots O(11^{f})$	$Ow - H(1w) \cdots O(11')$
0.70(3)	2.889(3)	2.21(3)	161(3)
N(6)—H(6)	$N(6) \cdots O(11^d)$	$H(6) \cdots O(11^d)$	$N(6) - H(6) \cdots O(11^d)$
0.96(3)	2.983(3)	2.03(3)	171(3)
Compound 3			
N(1) - H(1)	$N(1) \cdots O(32^e)$	$H(1) \cdots O(32^c)$	$N(1)$ — $H(1) \cdots O(32^{e})$
0.82(2)	3.048(5)	2.26(2)	163(3)
Ow—H(2w)	$Ow \cdots O(32^{b})$	$H(2w) \cdots O(32^b)$	$Ow - H(2w) \cdots O(32^{h})$
0.91(4)	2.770(4)	1.87(4)	168(3)
Ow—H(1w)	$\mathbf{Ow}\cdots\mathbf{O}(11^{f})$	$H(1w) \cdots O(11')$	$Ow - H(1w) \cdots O(11')$
0.70(3)	2.889(3)	2.21(3)	164(4)
N(6)—H(6)	$N(6) \cdots O(11^g)$	$H(6) \cdots O(11^g)$	$N(6)$ - $H(6)$ ··· $O(11^g)$
0.94(3)	2.995(3)	2.06(3)	175(3)

Table 7. Hydrogen bond scheme of the complexes (Angstrom and degrees)

 $a^{a}-x-1, -y, -z$   $b^{b}-x, -y, -z$   $c^{c}-x, -y, 1-z.$  $a^{d}1/2+x, 1/2-y, z-1/2.$ 

 $x^{-1/2}$ ,  $x^{-1/2}$ ,  $y^{-1/2}$ ,  $y^{-1/2}$ ,  $x^{-1/2}$ ,  $x^{-1/2}$ ,  $y^{-1/2}$ ,  $y^{-$ 

 $f_{1-x, -y, -z}$ 

 ${}^{g}x - 1/2, -y - 1/2, z + 1/2.$ 

and N(1)–C(2) bonds of the glycinate moiety and dihedral angles between the planes of carboxylic, peptide and phenyl groups illustrating this situation. The distances of the metal from the imidazole ring mean plane are -0.2238(6), 0.0593(5) and 0.0593(5) Å for 1, 2, and 3, respectively. The packing of these structures is mainly granted, in addition

to the van der Waals contacts, by hydrogen bonds (Table 7). In 1 these involve the NH and CO amide groups and the water molecules (Fig. 3), these connections run in the a and c directions; in 2 and 3 the imidazole NH group produces an additional hydrogen bond with the amide oxygen (Fig. 4); these linkages show no preferential directions.



Fig. 3. Projection of the unit cell of 1 on the ab plane.



Fig. 4. Projection of the unit cell of 3 on the ab plane.

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