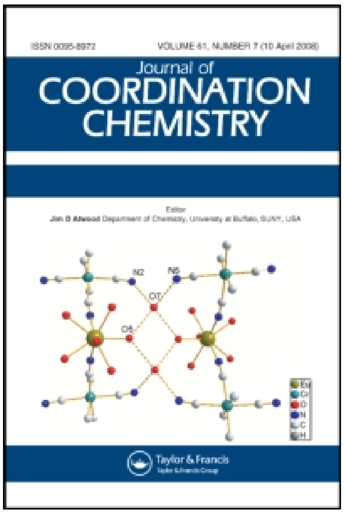

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Synthesis and spectroscopic properties of copper(II)-N-phthaloylglycinate derivatives of imidazole, methylimidazole, 1,10-phenanthroline and 2,2′,2″-terpyridine. Crystal structure of $[Cu(OH_2)_2(phen)(N\text{-}phthgly)]\ (NO_3)\cdot H_2O$ and $[Cu(terpy)(N\text{-}phthgly)_2]\cdot H_2O$

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A new series of copper(II) ternary complexes of N-phthaloylglycinate (N-phthgly) with imidazole (imi), methylimidazole (mimi), 1,10-phenanthroline (phen) and 2,2′,2″-terpyridine (terpy) have been synthesized and characterized. For two complexes $[Cu(terpy)(N\text{-}phthgly)_2]H_2O$ (**1**) and $[Cu(OH_2)_2(phen)(N\text{-}phthgly)]\ NO_3\cdot H_2O$ (**2**), crystal structures have been determined by X-ray diffraction. In complex **1**, the Cu(II) exhibits a distorted square-pyramidal geometry arising from coordination of three nitrogen atoms of 2,2′,2″-terpyridine and one oxygen of N-phthaloylglycinate in the basal plane and an oxygen atom of the second N-phthgly in the apex. In compound **2**, the copper(II) shows a distorted square-based pyramidal conformation with two nitrogens of the phenanthroline molecule, one water oxygen atom and a carboxylic oxygen of N-phthgly ligand forming the base; a second water is in the apex position. Water molecules and the carboxylate oxygens of the N-phthaloylglycinate molecules connect the molecules by H-bonds.

Keywords: Copper; N-Phthaloylglycinate; Ternary complexes; X-ray analysis

1. Introduction

Low-molecular weight ternary complexes of copper(II) prefer an N, O – donor set [1, 2]. They are abundant in living systems and involved in the transport of the metal ion through biological fluids and living tissues [3]. N-protected amino acidate complexes of copper (II) provide closely related structural and spectroscopic data which produce realistic model systems of many naturally occurring mixed ligand complexes.

Our interest in studying the coordination mode of N-phthaloylglycinate with first row transition metal ions has prompted us to investigate the synthesis, characterization

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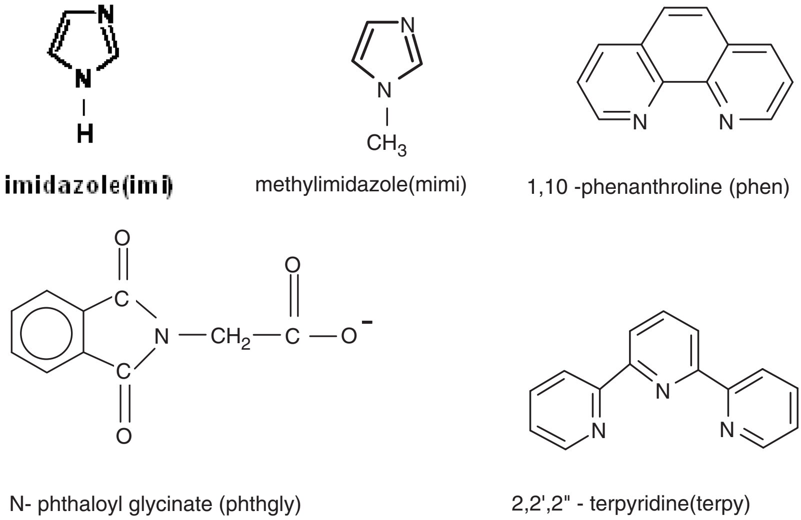

Scheme 1.

and X-ray crystal and molecular structure of some Cu(II) ternary complexes with imidazole, methylimidazole, 1,10-phenanthroline and 2,2′,2″-terpyridine (scheme 1). The crystal and molecular structures of **1** and **2** have been studied by X-ray diffraction.

2. Experimental

Materials: All chemicals were of the highest purity commercially available.

2.1. *Preparation of solid complexes*

2.1.1. Synthesis of [Cu(N-phthgly)$_2$(OH$_2$)$_4$]. [Cu(N-phthgly)$_2$(OH$_2$)$_4$] was prepared by adding an aqueous solution of copper(II) acetate monohydrate $CuAc_2 \cdot H_2O$ (0.40 g, 0.002 mol) to a hot methanol solution of the N-phthaloylglycinate (0.84 g, 0.004 mol). On cooling the solution a pale blue crystalline compound separated.

2.1.2. Synthesis of [Cu(phen)(N-phthgly)$_2$] · 2H$_2$O and [Cu(terpy)(N-phthgly)$_2$] · H$_2$O (1). [Cu(phen)(N-phthgly)$_2$] · 2H$_2$O and [Cu(terpy)(N-phthgly)$_2$] · H$_2$O (**1**) were prepared by dissolving 0.5 mmol of [Cu(N-phthgly)$_2$(OH$_2$)$_4$] in 30 cm^3 of 1 : 2 vol/vol mixture of H_2O and MeOH and mixing with 10 ml of a methanol solution (0.05 mol dm^{-3}) of 2,2′,2″-terpyridine or 1,10-phenanthroline. The green solutions of the Cu(II) ternary complexes were left covered for one week, after which green crystals of [Cu(terpy)(N-phthgly)$_2$] · H$_2$O and blue powder of [Cu(phen)(N-phthgly)$_2$] · 2H$_2$O have been separated.

2.1.3. Synthesis of [Cu(imi)$_2$(N-phthgly)$_2$] and [Cu(mimi)$_2$(N-phthgly)$_2$]. The ternary complexes of imidazole and methylimidazole were synthesized according to the same

Table 1. Elemental analyses, formula weights and melting points data for the copper(II) complexes.

Complex	F.W.	Found (Calcd)%			M.p. (°C)
		C	H	N	
$[Cu(OH_2)_4\ (N\text{-phthgly})_2]$	545.84	43.7	3.5	5.0	
Pale blue crystals	608.00	(44.0)	(3.7)	(5.1)	
$[Cu(imi)_2(N\text{-phthgly})_2]$		51.3	4.3	13.8	249
Blue crystals		(51.3)	(4.6)	(13.7)	
$[Cu(mimi)_2(N\text{-phthgly})_2]$	638.08	52.7	3.8	13.2	245
Blue crystals		(52.3)	(3.8)	(13.2)	
$[Cu(phen)(N\text{-phthgly})_2] \cdot 2H_2O$	688.07	56.8	3.2	8.2	275
Blue powder		(56.4)	(3.7)	(8.0)	
$[Cu(OH_2)_2(phen)(N\text{-phthgly})]\ (NO_3) \cdot H_2O$	546.90	47.3	3.8	10.2	247
Blue crystals		(47.5)	(3.9)	(9.9)	
$[Cu(terpy)(N\text{-phthgly})_2] \cdot H_2O$	725.14	58.0	3.6	9.7	289
Green crystals		(58.0)	(3.8)	(9.9)	

procedure by reacting 0.5 mmol of $[Cu(N\text{-phthgly})_2(OH_2)_4]$ with (1 mmol dm^{-3}) of imidazole or methylimidazle in a 1 : 2 molar ratio. Blue crystals of $[Cu(imi)_2(N\text{-phthgly})_2]$ and $[Cu(mimi)_2(N\text{-phthgly})_2]$ were obtained after three days.

2.1.4. Synthesis of $[Cu(OH_2)_2(phen)(N\text{-phthgly})](NO_3) \cdot H_2O$ (2). $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 0.002 mol) and 1,10-phenanthroline (0.36 g, 0.002 mol), were mixed in methanol. A methanol solution of phthaloylglycinate (0.41 g, 0.002 mol) was then added dropwisly to the mixture and the pH was adjusted to 8 by adding a few drops of NaOH aqueous solution. The green solution was left to stand for two weeks, at which time blue crystals of $[Cu(OH_2)_2(phen)(N\text{-phthgly})](NO_3) \cdot H_2O$ separated.

The elemental analyses for C, H and N for all copper(II) complexes are in accord with theoretical values (table 1).

2.2. *Instrumentation*

Elemental CHN analyses were carried out on a Carlo-Erba CHNS-O EA1108 elemental analyzer. Infrared spectra (KBr pellets) were recorded on a Nicolet 5PC FT-IR spectrometer. Thermogravimetry (TG) and differential thermal analysis (DTA) were performed using a Stanton STA 1500 Thermo analyzer with a heating rate of 10°C min^{-1} under N_2 atmosphere.

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

X-ray diffraction data were collected for compounds **1** and **2** at room temperature on different single crystal diffractometers (table 3) using Cu-Kα radiation. A standard reflection was monitored every 100, during any data collection processes, without significant variation. The data were corrected for Lorentz and polarization effects during the data reduction procedures [4, 5]. After isotropic refinement, the data were also corrected for absorption following the method of Walker and Stuart [6] with a program written by Gluzinski [7].

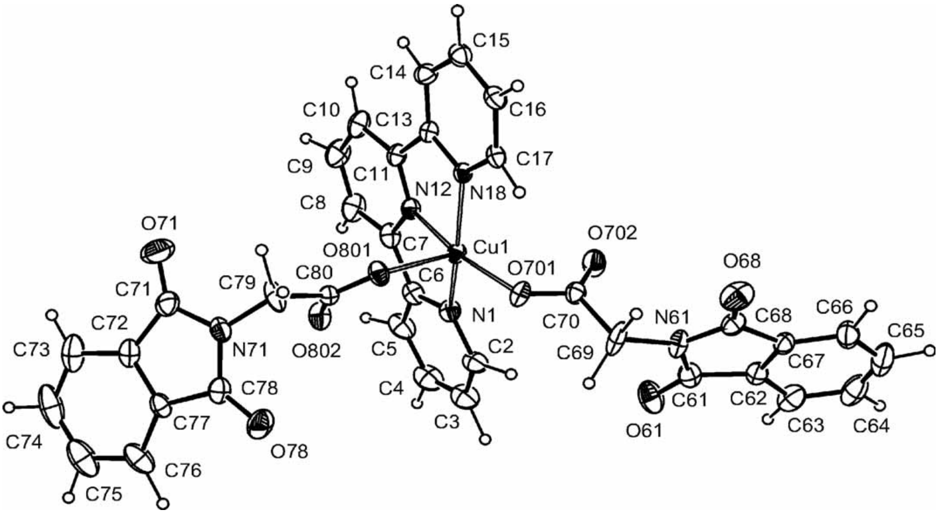

Figure 1. Projection of complex **1**.

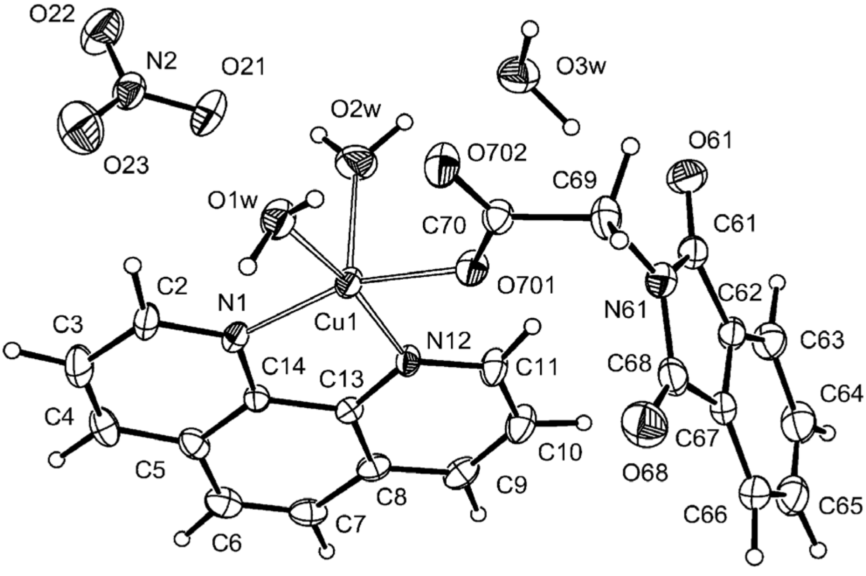

Figure 2. Projection of complex **2**.

All the structures were solved with SIR97 [8] and the refinements were carried out with SHELX97 [9] before with isotropic, and after with anisotropic, thermal factors. For the structures most hydrogen atoms were found in a final ΔF map, the remaining were put in their theoretical positions and all refined automatically.

The crystal data and relevant details concerning data collection and refinement are summarized in table 3. Selected bond distances and bond angles are summarized in tables 4 and 5 for the two complexes, respectively. The projections of the two complexes (**1** and **2**), in which the ellipsoids are at 30% probability, are in figures 1 and 2 [10]. The packing diagrams of the unit cell are in figures 3 and 4.

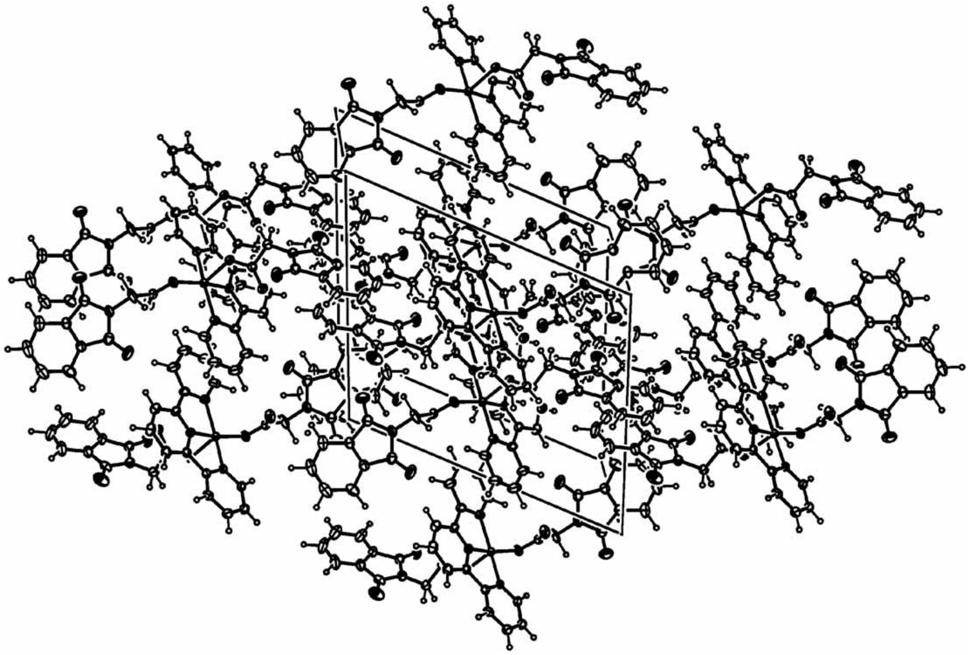

Figure 3. Packing of the unit cell of complex **1**.

3. Results and discussion

3.1. *Infrared spectra*

Relevant IR bands are reported in table 2. These infrared spectra are characterized by a broad band in the region 3458 cm^{-1} for $[Cu(phen)(N\text{-}phthgly)_2] \cdot 2H_2O$ and 3455 cm^{-1} for $[Cu(terpy)(N\text{-}phthgly)_2] \cdot H_2O$ which can be ascribed to the stretching vibration of water molecules present in the lattice or coordinated to the metal ion.

The IR spectrum of $[Cu(imi)_2(N\text{-}phthgly)_2]$ shows a distinct, strong band at 3202 cm^{-1}, which corresponds to the NH stretching vibration of imidazole. The presence of a very strong band in the range of 1625–1611 cm^{-1} for all complexes is typical for asymmetric vibration of the coordinated carboxylate group, confirming coordination of the N-phthaloylglycinate through the carboxylic oxygen [9]. In addition, the band in the range 1424–1417 cm^{-1} for all complexes can be ascribed to the symmetric vibration of the coordinated carboxylate group. Furthermore, two strong bands in the range 1775–1769 cm^{-1} and 1715–1705 cm^{-1} in the spectra of all complexes, can be assigned to the stretching vibration of two uncoordinated ketonic carbonyl groups $\upsilon(CO)_{ket}$, agreement with the X-ray crystal structure of the ternary complexes. This indicates that the coordination behavior of N-phthgly is unidentate through one carboxylic oxygen atom. Furthermore, complex **2** $[Cu(OH_2)_2(phen)(N\text{-}phthgly)]NO_3 \cdot H_2O$ is characterized by two bands, a strong band at 771 cm^{-1} and a very strong band at 1384 cm^{-1} attributed to $\nu_3(NO_3^-)$ and $\nu_t(NO_3^-)$ of NO_3^- group.

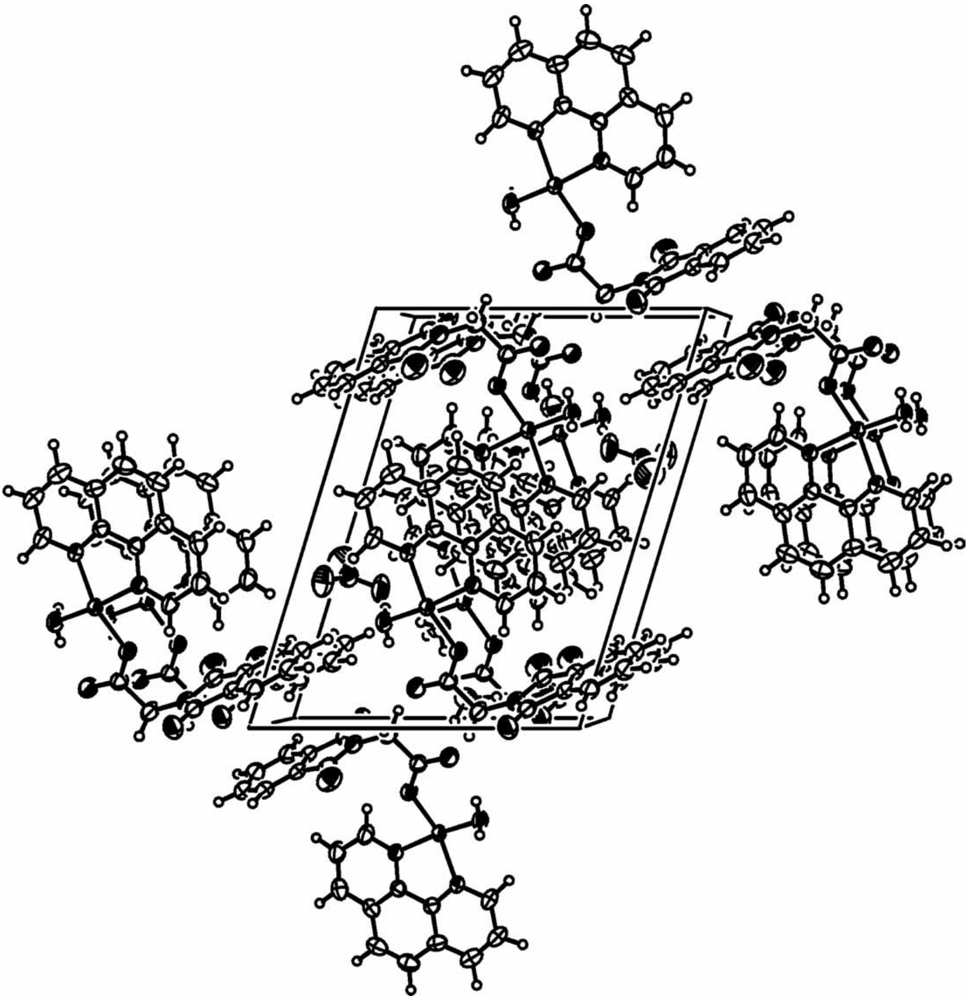

Figure 4. Packing of the unit cell of complex **2**.

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

Complex	ν(OH)	$\nu(\mathrm{CO})_{\mathrm{ket}}$	$\nu(\mathrm{COO})_{\mathrm{as}}$	$\nu(\mathrm{COO})_{\mathrm{s}}$
$[\mathrm{Cu(imi)_2(N\text{-}phthgly)_2}]$		1775s 1713s	1615s	1420s
$[\mathrm{Cu(mimi)_2(N\text{-}phthgly)_2}]$		1771s 1714s	1625s 1604s	1422s
$[\mathrm{Cu(phen)(N\text{-}phthgly)_2}] \cdot 2\mathrm{H_2O}$	3458	1769s 1713s	1613s	1419s
$[\mathrm{Cu(terpy)(N\text{-}phthgly)_2}] \cdot \mathrm{H_2O}$	3455	1769s 1705s	1619s	1424s
$[\mathrm{Cu(OH_2)_2(phen)(N\text{-}phthgly)}](\mathrm{NO_3}) \cdot \mathrm{H_2O}$	3462	1771s 1715s	1611s 1603s	1417s

Table 3. Experimental data for the crystallographic analyses.

Complex	**1**	**2**
Formula	$C_{35}H_{27}N_5O_8Cu \cdot H_2O$	$C_{22}H_{14}N_3O_4Cu \cdot 3H_2O \cdot NO_3$
MW	733.2	564.0
Crystal dimensions (mm^3)	$0.19 \times 0.29 \times 0.36$	$0.15 \times 0.22 \times 0.34$
Cell parameters (Å, °)		
a	15.731(2)	11.545(3)
b	14.500(3)	15.239(2)
c	7.853(3)	6.947(2)
α	92.26(4)	93.22(3)
β	99.06(3)	100.21(3)
γ	113.59(3)	73.03(3)
Cell determination:		
No. of reflections	31	24
θ range (°)	21.5–33.5	7.9–35.3
Cell volume (Å^3)	1610.7	1150.5
Symmetry	Triclinic	Triclinic
Space group	$P_{\bar{1}}$	$P_{\bar{1}}$
Collected reflections	4791	4325
Unique reflections, R int	4771, 0.0	4308, 0.0
Observed reflections [$F_o > 4\sigma(F_o)$]	4477	4000
2θ max. (°)	119.98	140.18
Indices range:		
h	−17/16	−14/14
k	−16/16	−18/18
l	−2/8	−1/8
No. of refined parameters	569	415
R_1	0.041	0.041
R_w	0.101	0.140
$w = 1./[\sigma^2 F_o^2 + \mathrm{KP})^2 + \mathrm{YP}]$	0.020	0.165
K, Y	0.0	1.7
GOF	2.76	0.63
$\Delta\rho_{\mathrm{min/max}}$	−0.49/0.31	−0.56/0.46
Diffractometer	SiemensAED	Enraf Nonius CAD4
Radiation	Cu-Kα	Cu-Kα
Lambda (Å)	1.5418	1.5418

3.2. *Thermogravimetric analysis*

Thermogravimetric (TG) analysis has been performed on the ternary complexes under investigation, with the aim of verifying the amount of solvent in such complexes. The TG plot for $[Cu(terpy)(N\text{-}phthgly)_2] \cdot H_2O$ (**1**) displays an initial slow weight loss of 2.75% in the range 50–150°C, in accord with the loss of one water molecule, likely of hydration. The TG plot of $[Cu(OH_2)_2(phen)(N\text{-}phthgly)]NO_3 \cdot H_2O$, displays two successive weight losses covering the 50–250°C range with a total loss of 9.78% which can be ascribed to the removal of three water molecules (one of hydration and two coordination).

3.3. *Crystal structure of [Cu(terpy)(N-phthgly)$_2$] · H$_2$O (1)*

The copper atom is in a distorted, square-based pyramid in complex **1**. Three nitrogen atoms of a capped 2,2′,2″-terpyridine molecule and one oxygen of a N-phthaloylglycinate group form the base while an oxygen of the second N-phthaloylglycinate molecule is the apex (figure 1). The geometry of this complex

Table 4. Selected bond distances (Å) and bond angles (°) for complex **1**.

Cul–O701	1.926(3)	C72–C73	1.389(6)
Cu1–O801	2.149(3)	C72–C77	1.372(5)
Cu1–N1	2.033(3)	C73–C74	1.388(10)
Cu1–N12	1.937(3)	C74–C75	1.358(9)
Cu1–N18	2.026(3)	C75–C76	1.372(7)
O61–C61	1.207(5)	C76–C77	1.373(6)
O68–C68	1.204(5)	C77–C78	1.480(5)
O71–C71	1.206(4)	C79–C80	1.533(4)
O78–C78	1.205(4)	N1–C2	1.341(4)
O701–C70	1.281(3)	N1–C6	1.357(5)
O702–C70	1.213(4)	N12–C7	1.348(5)
O801–C80	1.262(4)	N12–C11	1.331(4)
O802–C80	1.231(4)	N18–C13	1.350(4)
N61–C61	1.390(5)	N18–C17	1.344(5)
N61–C68	1.390(5)	C2–C3	1.383(6)
N61–C69	1.452(4)	C3–C4	1.368(7)
N71–C71	1.388(4)	C4–C5	1.375(6)
N71–C78	1.388(4)	C5–C6	1.388(6)
N71–C79	1.446(5)	C6–C7	1.472(5)
C61–C62	1.477(4)	C7–C8	1.388(5)
C62–C63	1.386(5)	C8–C9	1.372(6)
C62–C67	1.379(5)	C9–C10	1.387(7)
C63–C64	1.374(6)	C10–C11	1.387(5)
C64–C65	1.354(8)	C11–C13	1.486(5)
C65–C66	1.380(6)	C13–C14	1.378(5)
C66–C67	1.380(5)	C14–C15	1.380(6)
C67–C68	1.472(4)	C15–C16	1.371(5)
C69–C70	1.532(5)	C16–C17	1.372(5)
C71–C72	1.482(6)		
N12–Cu1–N18	79.8(1)	C73–C74–C75	121.8(8)
N1–Cu1–N18	156.3(1)	C74–C75–C76	120.9(6)
N1–Cu1–N12	79.8(2)	C75–C76–C77	117.8(5)
O801–Cu1–N18	89.7(2)	C72–C77–C76	122.3(5)
O801–Cu1–N12	95.8(2)	C76–C77–C78	130.0(3)
O801–Cu1–N1	104.3(2)	C72–C77–C78	107.7(3)
O701–Cu1–N18	99.4(2)	N71–C78–C77	106.3(3)
O701–Cu1–N12	166.5(3)	O78–C78–C77	129.0(3)
O701–Cu1–N1	97.7(1)	O78–C78–N71	124.7(6)
O701–Cu1–O801	97.7(2)	N71–C79–C80	114.0(5)
Cu1–O701–C70	118.6(3)	O802–C80–C79	119.0(6)
Cu1–O801–C80	124.1(5)	O801–C80–C79	113.1(5)

is comparable with those of other Ni-complexes [11–14]. Bond distances around the copper are as expected with a lengthening of the Cu–O801 apex bond, while the deformation of the square base, due to different coordinated ligands, is shown by the range of bond angles [79.8(1)–99.4(2)°]. The mean planes of the two N-phthaloylglycinate molecules form dihedral angles of 56.4(2)°, while those formed by the planar five-membered rings (N1–C6, C7–N12, C13–N18) are 4.6(2), 10.2(2) and 5.6(2)°, respectively. Inter- and intramolecular H-bonds are observed in the unit cell of complex **1** (table 6, figure 3). These involve the water and carboxylate oxygen atoms of the ligands, which connect the molecules in the crystal.

3.4. *Crystal structure of $[Cu(OH_2)_2(phen)(N\text{-}phthgly)](NO_3)\cdot H_2O$ (2)*

Figure 4 shows the content of the asymmetric unit which consists of $[Cu(OH_2)_2(phen)(N\text{-}phthgly)]^+$ cations, nitrate anions and water molecules.

Table 5. Selected bond distances (Å) and bond angles (°) for complex **2**.

Cu1–O701	1.954(2)	C5–C14	1.394(3)
Cu1–N1	2.009(2)	C6–C7	1.348(5)
Cu1–N12	2.010(2)	C7–C8	1.433(4)
Cu1–O1W	1.967(3)	C8–C9	1.405(4)
Cu1–O2W	2.193(4)	C8–C13	1.399(4)
O61–C61	1.201(4)	C9–C10	1.370(5)
O68–C68	1.209(4)	C10–C11	1.398(5)
O701–C70	1.266(3)	C13–C14	1.443(3)
O702–C70	1.239(4)	C61–C62	1.490(4)
N1–C2	1.335(3)	C62–C63	1.384(4)
N1–C14	1.351(4)	C62–C67	1.383(5)
N12–C11	1.332(3)	C63–C64	1.382(6)
N12–C13	1.350(3)	C64–C65	1.381(7)
N61–C61	1.390(3)	C65–C66	1.385(6)
N61–C68	1.401(5)	C66–C67	1.389(5)
N61–C69	1.451(4)	C67–C68	1.485(4)
C2–C3	1.397(5)	C69–C70	1.511(4)
C3–C4	1.365(5)	N2–O21	1.255(3)
C4–C5	1.403(4)	N2–O22	1.235(5)
C5–C6	1.439(5)	N2–O23	1.219(4)
O1W–Cu1–O2W	93.9(1)	C9–C10–C11	119.9(3)
N12–Cu1–O2W	95.3(1)	N12–C11–C10	121.7(2)
N12–Cu1–O1W	170.2(1)	N12–C13–C8	123.6(2)
N1–Cu1–O2W	99.2(1)	C8–C13–C14	120.5(2)
N1–Cu1–O1W	93.3(1)	N12–C13–C14	115.9(2)
N1–Cu1–N12	81.8(1)	C5–C14–C13	119.7(2)
O701–Cu1–O2W	96.6(1)	N1–C14–C13	116.3(2)
O701–Cu1–O1W	94.0(1)	N1–C14–C5	124.0(2)
O701–Cu1–N12	88.3(1)	O61–C61–N61	124.7(2)
O701–Cu1–N1	162.1(1)	N61–C61–C62	106.1(2)
Cu1–O701–C70	128.5(2)	O61–C61–C62	129.3(2)
Cu1–N1–C14	112.7(2)	C61–C62–C67	107.9(2)
Cu1–N1–C2	129.2(2)	C61–C62–C63	129.7(2)

Table 6. Possible intra- and intermolecular H-bonds.

Complex **1**			
O1W–H1W1 1.25(7)	O1W···O702 2.958(5)	H1W1···O702 1.75(6)	O1W–H1W1···O702 161(5)
C74–H74 0.91(5)	C74···O802i 3.220(6)	H74···O802i 2.38(6)	C74–H74···O802i 154(4)
C4–H4 0.90(4)	C4···O1Wii 3.429(7)	H4···O1Wii 2.53(4)	C4–H4···O1Wii 176(3)
O1W–H2W1 0.97(6)	O1W···O61iii 2.954(5)	H2W1···O61iii 1.99(6)	O1W–H2W1···O61iii 171(5)
C14–H14 0.97(3)	C14···O802iii 3.465(5)	H14···O802iii 2.50(3)	C14–H14···O802iii 176(3)
Complex **2**			
C11–H11 0.97(4)	C11···O701 2.964(4)	H11···O701 2.47(4)	C11–H11···O701 111(3)
O1W–H2W1 0.68(6)	O1W···O702 2.600(3)	H2W1···O702 1.96(6)	O1W–H2W1···O702 156(3)
O2W–H1W2 0.96(4)	O2W···O3W 2.746(4)	H1W2···O3W 1.83(4)	O2W–H1W2···O3W 158(3)
O2W–H2W2 0.65(5)	O2W···O21 2.885(49	H2W2···O21 2.29(4)	O2W–H2W2···O21 153(5)
O3W–H1W3 0.79(8)	O3W···O61 2.956(4)	H1W3···O61 2.23(7)	O3W–H1W3···O61 153(6)
C7–H7 0.86(5)	C7···O21i 3.308(5)	H7···O21i 2.49(5)	C7–H7···O21i 161(4)
O1W–H1W1 0.83(5)	O1W···O2ii 2.689(4)	H1W1···O21ii 1.86(5)	O1W–H1W1···O21ii 171(5)
O3W–H2W3 1.27(10)	O3W···O702iii 2.821(4)	H2W3···O702iii 1.60(10)	O3W–H2W3···O702 160(9)

(D = donor; A = acceptor; H = hydrogen); D–H (Å) D···A(Å) H···(Å) D–H···A (°).

Copper is five coordinate in a distorted, square-based pyramidal conformation with two nitrogens of the phenanthroline molecule, one water oxygen and a carboxylate oxygen of the N-phthaloylglycinate ligand as base; a second water oxygen is in the apex (figure 2). The distortion is clearly indicated by the angles around the copper which are in the range 81.8(1)–96.6(1)°. Comparable values were found in similar copper complexes [15, 16]. Other complexes with NO_3^- were reported [17–21]. All the rings are planar within error; the three rings of the phenanthroline molecule are a little bent toward each other so the mean central ring plane forms dihedral angles of 1.6(1) and 2.1(1)°. The mean phenanthroline plane is oriented with respect to the mean N-phthaloylglycinate ligand plane to form an angle of 73.7(1)°. In the crystal, the molecules are connected by H-bonds involving the water molecules, the NO_3^- group and the carboxylic oxygens of the N-phthaloylglycinate molecules.

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