

Four- and five-coordinate copper(II) complexes with *N*-(4,4-diphenyl-5-oxo-4,5-dihydro-1*H*-imidazol-2-yl)-glycine

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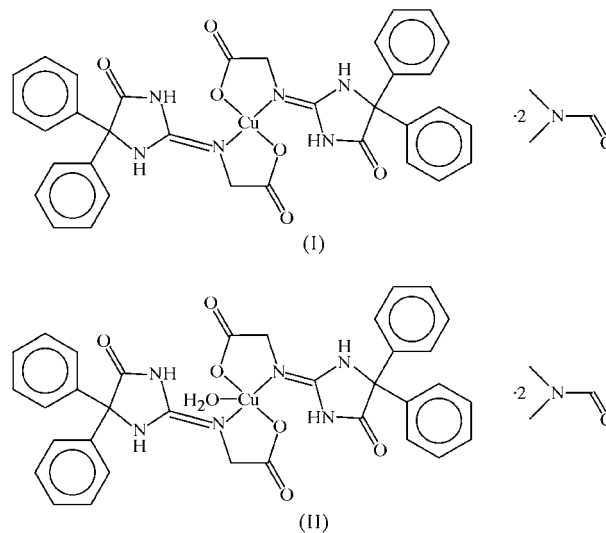
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The two title mononuclear compounds are four-coordinate bis[*N*-(5-oxo-4,4-diphenyl-4,5-dihydro-1*H*-imidazol-2-ylidene)glycinato]copper(II) dimethylformamide disolvate, [Cu(C₁₇H₁₄N₃O₃)₂]·2C₃H₇NO, (I), and five-coordinate aquabis[*N*-(5-oxo-4,4-diphenyl-4,5-dihydro-1*H*-imidazol-2-ylidene)glycinato]copper(II) dimethylformamide disolvate, [Cu(C₁₇H₁₄N₃O₃)₂(H₂O)]·2C₃H₇NO, (II). In (I), the Cu^{II} ion lies on an inversion centre with one-half of the complex molecule in the asymmetric unit, while in (II) there are two independent ligand molecules in the asymmetric unit, with the Cu^{II} ion and coordinated water molecule located on a general position. In both crystal structures, the complex molecules assemble in ribbons *via* N—H···O hydrogen-bond networks.

Comment

In our previous research, diphenyl- and arylideneimidazolin-4-one amino acids have been studied from the viewpoint of their binding to ionotropic (iGluRs) (Kieć-Kononowicz *et al.*, 1998) and/or metabotropic (iGluRs) receptors (Karolak-Wojciechowska & Kieć-Kononowicz, 2008). From information based on the model of ligand–receptor interactions with iGluRs (Karolak-Wojciechowska *et al.*, 2000), it was postulated that the presence of COO[−] ions in the amino acids studied was indispensable for binding (Karolak-Wojciechowska *et al.*, 2001). For this reason, we are currently focusing our attention on interactions between such amino acids and metals. As a first example, we obtained an interesting polymeric six-coordinate potassium complex with *o*-Cl-benzylideneimidazolin-4-one β-alanine and water molecules (Mrozek *et al.*, 2003). Recently, we obtained the two title Cu^{II} complexes, (I) and (II), with (4-oxo-5,5-diphenylimidazolidinyl)glycine (hereinafter abbreviated as DPGly), and present their crystal structures here.

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. In (I), the four-coordinate Cu^{II} ion lies on a crystallographic inversion centre and forms a square-planar



CuN₂O₂ unit (Table 1). The *N,O*-bidentate unit, belonging to the DPGly ligand, forms a planar five-membered ring. Even though the coordination numbers in structures (I) and (II) are not the same, in both compounds the Cu^{II} atom is coordinated by two *N,O*-bidentate units, with atoms O9 and N6 [and O49 and N46 in (II)] in a *trans* geometry. An increase in the coordination number of Cu^{II} from four in (I) to five in (II) is caused by the presence of a water molecule. This results not only in bond-length elongation in the coordination environment (Tables 1 and 3), but also in a shift of the Cu atom from the basal plane towards apical atom O1 (water molecule) in (II) [0.052 (5) Å for (I) and 0.1646 (11) Å for (II)]. Furthermore, the structure of (II) loses the centre of symmetry, with the space group changing from *P*2₁/*n* in (I) to *P*2₁ in (II). The distortion from ideal five-coordinate geometries can be best described by the degree of trigonality τ (Addison *et al.*, 1984). For a regular square-pyramidal (SQP) geometry the trigonality parameter is 0 and for a trigonal-bipyramidal (TBP)

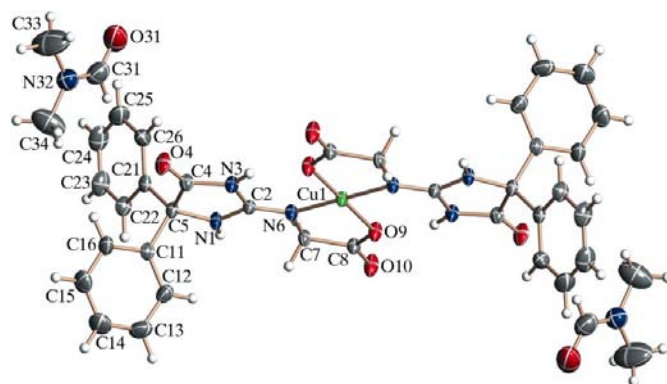


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are depicted as spheres of arbitrary radii. Unlabelled atoms are related to the corresponding labelled atoms by the symmetry code $(-x, -y, -z)$.

structure it increases to 1. In (II), $\tau = 0.114$, indicating a slightly distorted SQP coordination geometry around Cu^{II} .

The bond valences around the Cu^{II} atom in both structures were computed according to Brown (1994) and O'Keeffe & Brese (1991) as $\nu_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$, where R_{ij} is the bond-valence parameter (in the formal sense, it is the single-bond length between the i and j atoms) and d_{ij} is the observed bond length. In the present structures, the application of this correlation allows one to compare the relative importance of Cu–L bonds of Cu polyhedra, and to check the valence-sum rule for the Cu^{II} atom (Brown, 2002). According to Shields *et al.* (2000), $R_{\text{Cu-N}}$ and $R_{\text{Cu-O}}$ were taken as 1.716 and 1.657 Å, respectively, for (I), and 1.705 and 1.652 Å for (II). The

estimated bond valences of the Cu^{II} atom show that, in both structures, the equatorial Cu–N bonds are distinctly stronger than the equatorial Cu–O bonds [$\nu_{\text{Cu-N}} = 0.530$ valence units (v.u.) and $\nu_{\text{Cu-O}} = 0.489$ v.u. in (I), and $\nu_{\text{Cu-N(av)}} = 0.485$ v.u. and $\nu_{\text{Cu-O(av)}} = 0.439$ v.u. in (II)]. The valence of the axial Cu–O1 bond in (II) is 0.155 v.u. Finally, the valences of the four- and five-coordinate Cu atoms are consistent with the valence-sum rule ($V_i = \sum \nu_{ij}$), which gives $V_{\text{Cu}} = 2.037$ for (I) and 2.003 for (II).

The dihedral angles between the planes of the five-membered imidazole ring and the respective phenyl rings located on atoms C5 and C45 in (II) are not equal [76.76 (13)° for the C11–C16 ring, 57.34 (10)° for C21–C26, 67.04 (9)° for C51–C56 and 64.72 (11)° for C61–C66], while in (I) they are equal within experimental error [68.78 (14) and 69.26 (14)° for the corresponding C11–C16 and C21–C26 rings, respectively].

In the structure of (I), intramolecular $\text{N3-H3} \cdots \text{O9}(-x, -y, -z)$ hydrogen bonds join two DPGly ligands. This bond generates an $S(6)$ graph-set motif (Etter *et al.*, 1990) in the plane of the N,O -bidentate units. The complex molecules are connected together by $\text{N1-H1} \cdots \text{O10}(1-x, -y, -z)$ hydrogen bonds, forming rings of graph-set $R_2^2(14)$. These rings construct ribbons running along the a axis which are slightly inclined with respect to the ac plane (Fig. 3 and Table 2). The distance between two parallel ribbons is equal to the b -axis value [14.075 (6) Å], but another ribbon, oppositely inclined to the ac plane, is present at $0.5b$. Between these two ribbons there is enough space for the location of all the phenyl

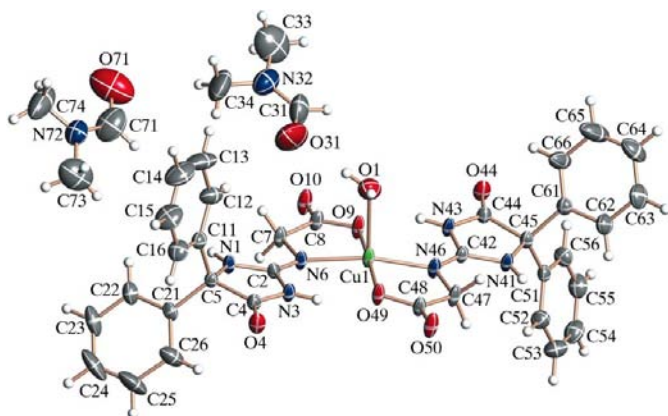


Figure 2
View of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are depicted as spheres of arbitrary radii. For clarity, only the major component of the disordered atoms is shown.

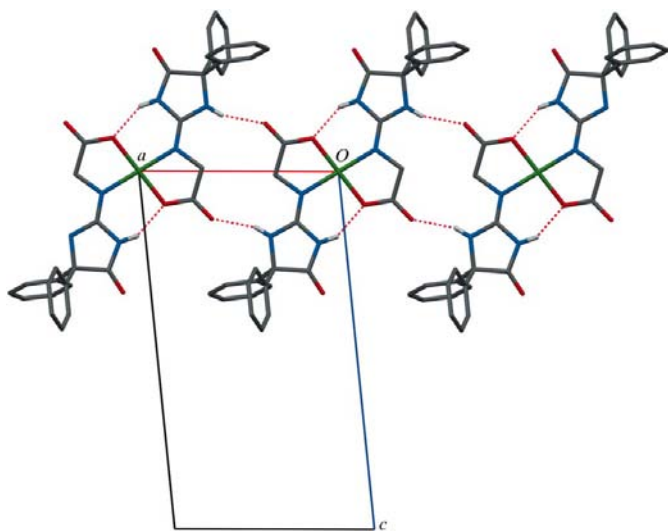


Figure 3
Hydrogen-bonded polymeric ribbons in (I), running along the [100] direction and viewed down the [010] direction. Hydrogen bonds are drawn as dashed lines and DMF molecules have been omitted for clarity.

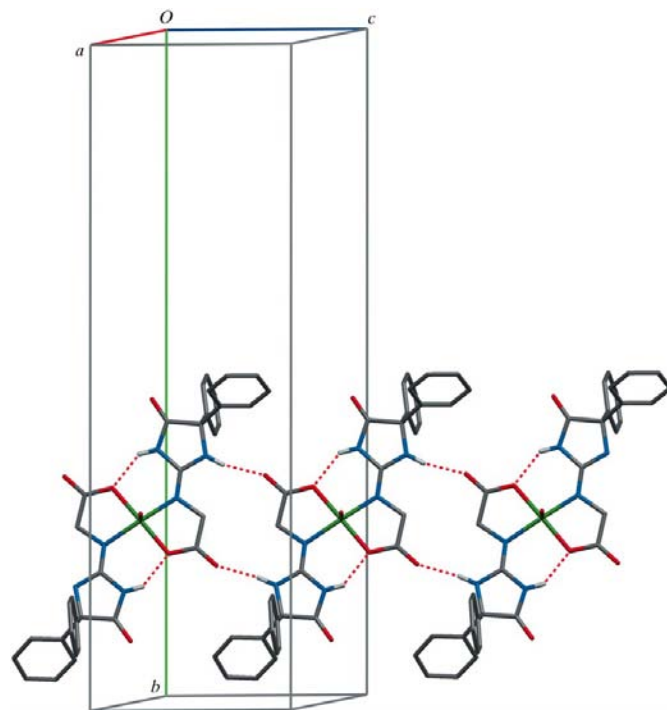


Figure 4
Hydrogen-bonded polymeric ribbons in (II), running along the [001] direction. Hydrogen bonds are drawn as dashed lines and DMF molecules have been omitted for clarity.

rings from the DPGly molecules and the respective number of dimethylformamide (DMF) solvent molecules. The DMF molecules bridge successive ribbons through noncovalent interactions in the crystal structure of (I). Therefore, from one site, DMF atom O31 is involved in a weak C71—H71 \cdots O31($-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$) interaction with glycine atom C7 of one ribbon, while the other imidazolidinone carbonyl O atom from the second ribbon participates in a weak C34—H342 \cdots O4($-x, -y, 1 - z$) interaction with a DMF C atom [3.514 (8) Å].

Analogous intra- and intermolecular N—H \cdots O hydrogen bonds are also recognized in the structure of (II) (Fig. 4 and Table 4), with the final ribbons running along the *c* axis and with the distance between parallel ribbons amounting to the *a*-axis value [8.7305 (3) Å]. The space between the ribbons contains not only the phenyl rings from the DPGly molecules and the respective number of DMF solvent molecules, but also a ligand water molecule. The DMF solvent molecules in (II) are anchored differently than in (I). Both DMF molecules are hydrogen bonded to the coordinated water *via* relevant O1—H1W \cdots O31 and O1—H2W \cdots O41($x, y, z + 1$) interactions. Additionally, weak hydrogen-bond C7—H7B \cdots O71($x - 1, y, z$) interactions involving one DMF molecule maintain the parallel ribbons. It is worth mentioning that one of the two imidazolidinone carbonyl O atoms in (II) (O44) is involved in an intermolecular interaction, creating a relatively strong C24—H24 \cdots O44($-x, \frac{1}{2} + y, 1 - z$) hydrogen bond to a neighbouring ribbon at an angle of 170°. Due to this extended interaction, parallel ribbons form a helix down the *b* axis.

Experimental

To obtain crystals of the title complexes, the method described by Dziemidowicz-Borys (2006) was adapted. Locally synthesized *N*-(4-oxo-5,5-diphenylimidazolidinyl)glycine (Kieć-Kononowicz *et al.*, 1995) was used as the ligand for complex formation. A solution of CuCl₂·2H₂O (9 mg, 0.052 mmol) in DMF (2 ml) was added to *N*-(4-oxo-5,5-diphenylimidazolidinyl)glycine (16 mg, 0.052 mmol) dissolved in warmed DMF (2 ml). The resulting green–blue solution was left at room temperature for a couple of days with limited air contact. After two weeks, violet crystals of (I) appeared, which were carefully filtered off. From the filtrate left in contact with air, a few blue crystals of (II) were obtained after a further two weeks.

Compound (I)

Crystal data

[Cu(C ₁₇ H ₁₄ N ₃ O ₃) ₂] ₂ ·2C ₃ H ₇ NO	<i>V</i> = 2039.3 (15) Å ³
<i>M_r</i> = 826.37	<i>Z</i> = 2
Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.987 (4) Å	<i>μ</i> = 0.60 mm ⁻¹
<i>b</i> = 14.075 (6) Å	<i>T</i> = 291 K
<i>c</i> = 16.208 (7) Å	0.2 × 0.1 × 0.05 mm
<i>β</i> = 95.913 (6)°	

Data collection

Bruker SMART APEXII CCD diffractometer	28748 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	3590 independent reflections
<i>T_{min}</i> = 0.924, <i>T_{max}</i> = 0.979	2815 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.052

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.051	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.130	$\Delta\rho_{\max}$ = 0.67 e Å ⁻³
<i>S</i> = 1.14	$\Delta\rho_{\min}$ = -0.27 e Å ⁻³
3590 reflections	
269 parameters	

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1—O9	1.922 (2)	O9—C8	1.292 (3)
Cu1—N6	1.951 (3)	O10—C8	1.218 (4)
O4—C4	1.203 (4)		
O9—Cu1—N6	84.32 (9)	O9—Cu1—N6 ⁱ	95.68 (9)

Symmetry code: (i) $-x, -y, -z$.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O10 ⁱⁱ	0.78 (4)	2.02 (4)	2.768 (4)	160 (3)
N3—H3 \cdots O9 ⁱ	0.83 (4)	1.91 (3)	2.663 (3)	149 (3)
C7—H71 \cdots O31 ⁱⁱⁱ	0.97	2.35	3.268 (5)	157

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, -y, -z$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Compound (II)

Crystal data

[Cu(C ₁₇ H ₁₄ N ₃ O ₃) ₂ (H ₂ O)]·2C ₃ H ₇ NO	<i>β</i> = 118.102 (4)°
<i>M_r</i> = 844.38	<i>V</i> = 2091.15 (12) Å ³
Monoclinic, <i>P</i> ₂ ₁	<i>Z</i> = 2
<i>a</i> = 8.7305 (3) Å	Mo <i>K</i> α radiation
<i>b</i> = 30.0213 (5) Å	<i>μ</i> = 0.59 mm ⁻¹
<i>c</i> = 9.0447 (2) Å	<i>T</i> = 293 K
	0.30 × 0.25 × 0.22 mm

Data collection

Kuma KM-4 CCD diffractometer	21287 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	7171 independent reflections
<i>T_{min}</i> = 0.825, <i>T_{max}</i> = 0.882	6447 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R_{int}</i> = 0.016

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.026	$\Delta\rho_{\max}$ = 0.20 e Å ⁻³
<i>wR</i> (<i>F</i> ²) = 0.066	$\Delta\rho_{\min}$ = -0.17 e Å ⁻³
<i>S</i> = 1.00	Absolute structure: Flack (1983), with 1462 Friedel pairs
7171 reflections	Flack parameter: 0.00 (1)
545 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 3

Selected geometric parameters (Å, °) for (II).

Cu1—O1	2.341 (3)	Cu1—N46	1.971 (2)
Cu1—O9	1.9523 (15)	O9—C8	1.273 (3)
Cu1—O49	1.9606 (15)	O10—C8	1.234 (3)
Cu1—N6	1.9751 (17)		
O1—Cu1—O9	93.86 (10)	O9—Cu1—N6	83.46 (7)
O1—Cu1—O49	92.32 (8)	O9—Cu1—N46	96.18 (8)
O1—Cu1—N6	92.21 (8)	O49—Cu1—N6	95.96 (7)
O1—Cu1—N46	100.81 (9)	O49—Cu1—N46	82.99 (7)
O9—Cu1—O49	173.81 (9)	N6—Cu1—N46	166.97 (9)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O50 ⁱ	0.86	1.99	2.828 (2)	166
N41—H41...O10 ⁱⁱ	0.86	1.98	2.821 (2)	167
O1—H1W...O31	0.84 (4)	1.99 (4)	2.828 (6)	178 (4)
O1—H2W...O71 ⁱⁱ	0.88 (5)	1.90 (4)	2.763 (5)	168 (4)
N3—H3...O49	0.86	1.93	2.676 (2)	144
N43—H43...O9	0.86	1.96	2.698 (3)	143
C24—H24...O44 ⁱⁱⁱ	0.93	2.53	3.453 (4)	170

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, z + 1$; (iii) $-x, y + \frac{1}{2}, -z + 1$.

In (I), the H atoms attached to atoms N1 and N3 were located in a difference Fourier map and their positions and displacement parameters were refined freely. In (II), H atoms attached to N atoms were placed in idealized positions and constrained to ride on their parent atoms, with N—H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. For both compounds, phenylene and methylene H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 and 0.97 Å, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The methyl H atoms in the DMF molecules were found in a difference Fourier map and were included using an AFIX 137 command (SHELXTL; Bruker, 2003), with C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. One of the DMF molecules in (II) showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.65 and 0.35.

Data collection: SMART (Bruker, 2002) for (I); CrysAlis CCD (Oxford Diffraction, 2006) for (II). Cell refinement: SAINT-Plus (Bruker, 2003) for (I); CrysAlis RED (Oxford Diffraction, 2006) for (II). Data reduction: SAINT-Plus for (I); CrysAlis RED for (II). For both compounds, program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3059). Services for accessing these data are described at the back of the journal.

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