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(Glycylglycinato-κ^3O,N,N')(2-methyl-1*H*-benzimidazole-κN^3)copper(II) trihydrate

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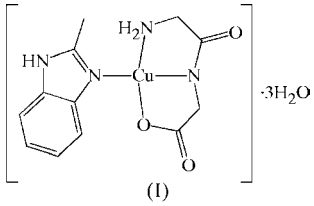
In the title compound, $[Cu(C_4H_6N_2O_3)(C_8H_8N_2)]\cdot 3H_2O$, the Cu^{II} atom is coordinated in a square-planar manner by one O atom and three N atoms from glycylglycinate and 2-methylbenzimidazole ligands. The ternary complexes assemble into one-dimensional chains through C—H$\cdots\pi$ interactions and direct N—H$\cdots$O hydrogen bonding, as well as into hydrogen-bonded water helices with branches which also link the complex chains into a three-dimensional supramolecular structure.

Comment

Dipeptide–metal complexes have attracted interest because they can act as model complexes to study metal–protein interactions (Tasiopoulos *et al.*, 1998, 2000, 2002). Some ternary complexes of metal ions with peptides and other ligands can cleave DNA (García-Raso *et al.*, 2003). To date, many crystal structures of peptide–metal complexes have been studied, with some of them investigated for their magnetic properties (García-Raso *et al.*, 1998, 2002). As peptide–metal complexes can form abundant hydrogen bonds, by which the complexes possibly interact with proteins and further affect their structures and functions, the strutures and weak interactions of peptide–metal complexes have attracted our interest. During our experiment, the title compound, [Cu(gg)(mbenz)]·3H_2O (H_2gg is glycylglycine and mbenz is 2-methylbenzimidazole), (I), was synthesized and its crystal structure determined.



(I)

Compound (I) consists of a ternary complex and three solvent water molecules. In the ternary complex, the Cu atom is coordinated by one O atom and three N atoms, *i.e.* with the glycylglycinate ligand providing one O and two N atoms and the methylbenzimidazole ligand providing one N atom, forming a square-planar geometry. This square-planar coordination environment is in good agreement with that of [Cu(gg)(bzim)]·3H_2O (bzim is benzimidazole; García-Raso *et al.*, 1996), (II). However, in (I), due to the steric effect of the methyl group of the 2-methylbenzimidazole ligand, the glycylglycinate (N1/N2/O1–O3/C1–C4) and 2-methylbenzimidazole (N3/N4/C5–C12) ligands are twisted with a dihedral angle of 53.8 (1)°, in contrast with (II), where the dihedral angle is 19.0 (1)°.

The ternary complexes assemble in an antiparallel and alternating fashion into one-dimensional chains along the *b* axis through C—H$\cdots\pi$ interactions and N—H$\cdots$O hydrogen bonds (N1—H1*B*$\cdots$O2^{v}; see Table 2) between neighbouring

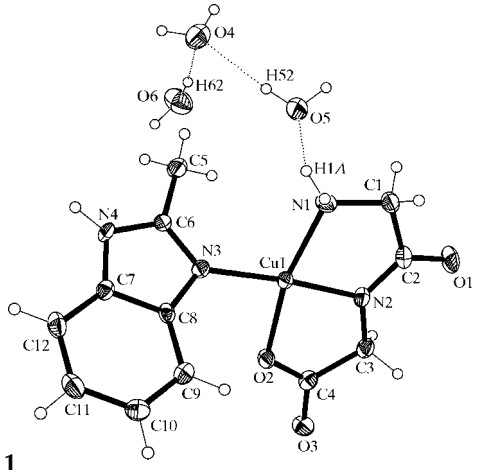


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 30% probability level. Dotted lines indicate hydrogen bonds.

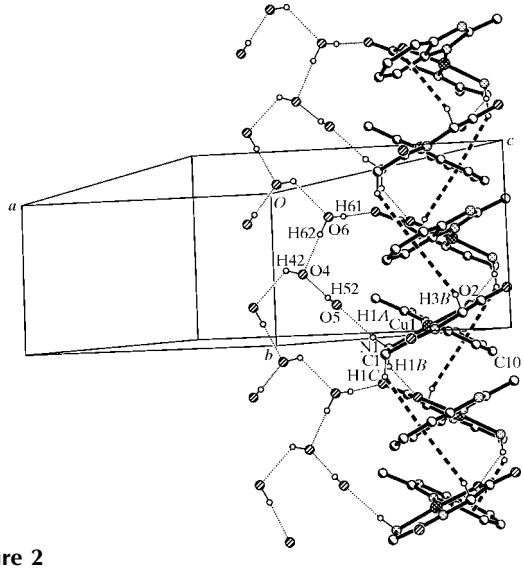


Figure 2
The one-dimensional complex chain built from C—H$\cdots\pi$ interactions (dashed lines) and direct hydrogen bonding (dotted lines). The hydrogen-bonded water helix with branches is also shown. H atoms not involved in the hydrogen bonding have been omitted for clarity.

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complexes; chains of water molecules link the one-dimensional complex chains into a three-dimensional supramolecular structure (Fig. 2). The two C—H···π (C1—H···$Cg1^{v}$ and C3—H···$Cg1^{i}$; $Cg1$ is the centroid of the C7–C12 ring) interactions are obviously different from what was seen in (II), where only the water chains take part in constructing one-dimensional chains of the [Cu(gg)(bzim)] complexes. Evidently, the C—H···π interactions and direct hydrogen bonding result from the conformational change, *i.e.* the larger twist between the peptide and benzimidazole groups in (I) than in (II), because of the steric effect of the methyl group of 2-methylbenzimidazole. This steric effect also changes the arrangement of the water molecules. In (I), the three water molecules are hydrogen bonded into a water helix with branches (Fig. 2), in contrast to the smooth helix in (II). Therefore, the steric effect of a methyl group can affect the molecular structure, which further changes the packing mode of the complexes in the crystal.

Experimental

Compound (I) was synthesized by adding 2-methylbenzimidazole (0.53 mmol) to a hot aqueous solution (20 ml) of aquaglycylglycinatocopper(II) (0.52 mmol), synthesized according to the method of Sato *et al.* (1986). The mixture was then stirred at 353 K for 30 min, cooled to room temperature with stirring overnight and filtered. Purple crystals of (I) were obtained from the filtrate at room temperature over a period of 10 d (yield 42.9%).

Crystal data

$[Cu(C_4H_6N_2O_3)(C_8H_8N_2)]\cdot 3H_2O$
M_r = 379.86
Monoclinic, $P2_1/c$
a = 13.094 (5) Å
b = 7.840 (3) Å
c = 18.854 (5) Å
β = 126.182 (18)°
V = 1562.2 (9) Å^3
Z = 4
D_x = 1.615 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.44 mm^{-1}
T = 298 (2) K
Needle, purple
0.40 × 0.10 × 0.03 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.598, T_{max} = 0.958
6158 measured reflections
2754 independent reflections
2461 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.127
S = 1.23
2754 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 2.2578P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

H atoms attached to C and N atoms were placed in geometrically idealized positions, with Csp^2—H = 0.93 Å, methyl Csp^3—H = 0.96 Å, methylene Csp^3—H = 0.97 Å, Nsp^2—H = 0.86 Å and Nsp^3—H = 0.90 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C,N), or 1.5U_{eq}(C) for methyl H atoms. H atoms attached to O atoms were allowed for as riding, with O—H = 0.85–0.87 Å and U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.884 (4)	Cu1—O2	1.999 (3)
Cu1—N3	1.964 (4)	Cu1—N1	2.011 (4)
N2—Cu1—N3	174.91 (15)	N2—Cu1—N1	83.35 (16)
N2—Cu1—O2	82.62 (14)	N3—Cu1—N1	101.72 (15)
N3—Cu1—O2	92.31 (13)	O2—Cu1—N1	165.96 (14)

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C7–C12 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O6—H62···O4	0.87	2.01	2.867 (6)	171
O6—H61···O3^{i}	0.85	2.05	2.892 (5)	174
O5—H52···O4	0.85	2.10	2.934 (5)	168
O5—H51···O1^{ii}	0.85	1.93	2.756 (5)	163
O4—H42···O6^{iii}	0.85	2.25	2.787 (6)	121
O4—H41···O1^{iv}	0.85	1.99	2.796 (5)	158
N4—H4···O3^{iv}	0.86	1.91	2.773 (5)	176
N1—H1*B*···O2^{v}	0.90	2.25	3.021 (5)	144
N1—H1*A*···O5	0.90	2.14	2.956 (5)	151
C1—H1*C*···$Cg1^{v}$	0.97	2.77	3.604 (6)	144
C3—H3*B*···$Cg1^{i}$	0.97	2.81	3.547 (6)	133

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, -y+2, -z+2$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3003). Services for accessing these data are described at the back of the journal.

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