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A redetermination of (N^9-adenine-κN)aqua[glycylglycinato(2−)-$\kappa^3 N,N',O$]copper(II)

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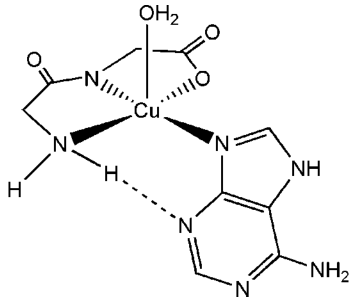
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.007 Å; R factor = 0.059; wR factor = 0.166; data-to-parameter ratio = 13.5.

In the title complex, $[Cu(C_4H_6N_2O_3)(C_5H_5N_5)(H_2O)]$, the Cu^{II} atom is five-coordinated in a square-pyramidal geometry by a tridentate glycylglycinate ligand (glygly), an N atom from an adenine ligand (Hade) and a water molecule in the apical position. The Hade coordination is reinforced by an intramolecular hydrogen-bonding interaction. A much lower precision structure has already been determined using intensities collected by the film method [Tomita, Izumo & Fujiwara (1973). *Biochem. Biophys. Res. Commun.* **54**, 96–99].

Related literature

The reported molecular recognition mode was not described previously (Tomita *et al.*, 1973). In constrast, it has long been known that in the closely related $[Cu(glygly)(9Meade)(H_2O)]\cdot 4H_2O$ (9Meade is 9-methyladenine; Kistenmacher *et al.*, 1976), the Cu—N(9Meade) bond is reinforced by one $N_{amine}—H\cdots O$(apical/aqua) intramolecular bond, but there is not a direct glygly-9-methyladenine intramolecular interligand interaction. For related literature, see: Addison *et al.* (1984).



Experimental

Crystal data

$[Cu(C_4H_6N_2O_3)(C_5H_5N_5)(H_2O)]$
M_r = 346.80
Triclinic, $P\overline{1}$
a = 6.919 (3) Å
b = 7.617 (3) Å
c = 12.060 (5) Å
α = 93.213 (7)°
β = 94.640 (6)°
γ = 94.614 (7)°
V = 630.2 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.76 mm^{-1}
T = 273 (2) K
0.33 × 0.13 × 0.08 mm

Data collection

Bruker SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004) T_{min} = 0.594, T_{max} = 0.872
6720 measured reflections
2566 independent reflections
1816 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.166
S = 1.04
2566 reflections
190 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.99 e Å^{-3}
$\Delta\rho_{min}$ = −1.41 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···O13^{i}	0.82	2.04	2.740 (6)	143
O1—H1A···O12^{ii}	0.83	2.33	2.735 (6)	111
N12—H12B···O13^{iii}	0.86	2.24	2.978 (7)	143
N12—H12A···N3	0.86	2.29	2.927 (6)	131
N7—H7···O12^{iv}	0.90	1.78	2.674 (5)	170
N6—H6B···N1^{v}	0.87	2.16	2.996 (6)	162

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z$; (iv) $-x+1, -y+1, -z+1$; (v) $-x-1, -y, -z+1$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2382).

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supplementary materials

Acta Cryst. (2007). E**63**, m1598 [**doi:10.1107/S1600536807021605**]

A redetermination of (N^9-adenine-κ*N*)aqua[glycylglycinato(2-)-κ^3N,N',O]copper(II)

M. P. Brandi-Blanco, B. Dumet-Fernandes, J. M. González-Pérez and D. Choquesillo-Lazarte

Comment

The molecular structure of the title compound, (I) (Fig.1), has been reported previously (Tomita *et al.*, 1973) but the prescision of the current structure determination is vastly improved. The Cu^{II} ion exhibits a square base pyramidal 4 + 1 coordination, τ parameter 0.26 (Addison *et al.*, 1984). An intra-molecular interligand H-bonding interaction, namely N—H(glygly)···N3(Hade), reinforces the Cu—N9(Hade) coordination bond, thus contributing to the molecular recognition pattern between the Cu-dipeptide chelate and the adenine, which retains its dissociable H atom on N7. In the crystal structure, molecules are linked through N—H···N, N—H···O and O—H···O hydrogen bonds, forming a three-dimensional network (Fig. 2).

Experimental

To a solution resulting from the reaction of $Cu_2CO_3(OH)_2$ (0.5 mmol) in 90 ml of water, an aqueous solution (60 ml) of the base pair adenine:thymine (1 mmol of each base) was added. The evaporation at r.t. yields crystals of the new mixed-ligand complex $[Cu^{II}(C_4H_6N_2O_3)(C_5H_5N_5)(H_2O)]$. The same compound was also obtained using the free base adenine instead of the complementary pair.

Refinement

Aqua and amine H atoms were located in a difference map and refined as riding, in their as-found positions. Other H atoms were positioned geometrically and treated as riding with C—H = 0.95–0.99 Å. All U_{iso}(H) values were constrained to be 1.2 times U_{eq} of the carrier atom. The highest peak in the final difference Fourier of 0.99 e $Å^{-3}$ is 0.97Å from Cu1 and the deepest hole of −1.40 e $Å^{-3}$ is 0.96Å from Cu1

Figures

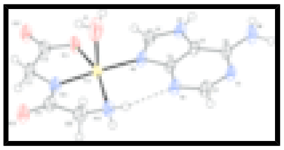

Fig. 1. The molecular structure of (I), showing the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as spheres of arbitrary radii. The dashed line indicates an intramolecular hydrogen bond.

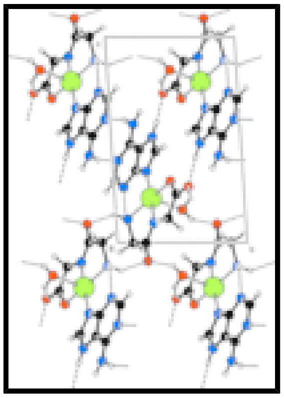

Fig. 2. A view, along the *a* axis, of the molecular packing of (I). The intermolecular hydrogen bonds are shown as dashed lines.

(N^9-adenine-κ*N*)aqua[glycylglycinato(2-)-\ κ^3*N*,*N*',*O*]copper(II)

Crystal data

$[Cu(C_4H_6N_2O_3)(C_5H_5N_5)(H_2O)]$	$Z = 2$
$M_r = 346.80$	$F_{000} = 354$
Triclinic, $P\overline{1}$	$D_x = 1.828$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
a = 6.919 (3) Å	Cell parameters from 806 reflections
b = 7.617 (3) Å	θ = 2.7–28.5°
c = 12.060 (5) Å	μ = 1.76 mm^{-1}
α = 93.213 (7)°	*T* = 273 (2) K
β = 94.640 (6)°	Plate, blue
γ = 94.614 (7)°	0.33 × 0.13 × 0.08 mm
V = 630.2 (5) Å^3	

Data collection

Bruker SMART 1000 diffractometer	2566 independent reflections
Radiation source: fine-focus sealed tube	1816 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.068$
T = 273(2) K	$\theta_{max} = 26.4°$
ω scans	$\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	$h = -8\rightarrow8$
$T_{min} = 0.594$, $T_{max} = 0.872$	$k = -9\rightarrow9$
6720 measured reflections	$l = 0\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.166$	$w = 1/[\sigma^2(F_o^2) + (0.087P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
2566 reflections	$\Delta\rho_{max} = 0.99$ e Å^{-3}
190 parameters	$\Delta\rho_{min} = -1.40$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.36815 (9)	0.28116 (9)	0.21733 (5)	0.0320 (3)
N1	−0.3262 (6)	0.0393 (6)	0.3990 (3)	0.0308 (10)
C2	−0.2523 (8)	0.0108 (8)	0.3017 (4)	0.0337 (13)
H2	−0.3304	−0.0627	0.2490	0.040*
N3	−0.0810 (6)	0.0733 (6)	0.2693 (3)	0.0336 (11)
C4	0.0252 (7)	0.1750 (7)	0.3516 (4)	0.0244 (10)
C5	−0.0351 (7)	0.2129 (7)	0.4549 (4)	0.0255 (11)
C6	−0.2217 (7)	0.1437 (7)	0.4798 (4)	0.0282 (11)
N6	−0.3000 (7)	0.1763 (7)	0.5760 (4)	0.0415 (12)
H6A	−0.2466	0.2336	0.6363	0.050*
H6B	−0.3954	0.1102	0.5982	0.050*
N7	0.1150 (6)	0.3158 (6)	0.5138 (3)	0.0313 (10)
H7	0.1034	0.3582	0.5842	0.038*
C8	0.2554 (8)	0.3370 (7)	0.4460 (4)	0.0345 (13)
H8	0.3733	0.4029	0.4664	0.041*
N9	0.2114 (6)	0.2550 (6)	0.3458 (3)	0.0295 (10)
N11	0.5310 (6)	0.2917 (6)	0.0976 (3)	0.0334 (11)
C11	0.7143 (8)	0.3996 (7)	0.1182 (4)	0.0324 (12)
H11A	0.7187	0.4940	0.0675	0.039*
H11B	0.8218	0.3285	0.1064	0.039*
C12	0.7302 (7)	0.4758 (7)	0.2375 (4)	0.0297 (11)
O11	0.5924 (5)	0.4369 (5)	0.2984 (3)	0.0368 (9)
O12	0.8795 (5)	0.5740 (5)	0.2714 (3)	0.0413 (10)
C21	0.4650 (8)	0.2204 (7)	−0.0009 (4)	0.0335 (13)

O13	0.5490 (6)	0.2262 (5)	−0.0904 (3)	0.0445 (11)
C22	0.2650 (8)	0.1224 (8)	−0.0016 (4)	0.0400 (14)
H22A	0.1673	0.1927	−0.0347	0.048*
H22B	0.2606	0.0119	−0.0462	0.048*
N12	0.2224 (7)	0.0868 (6)	0.1136 (4)	0.0387 (12)
H12A	0.0982	0.0717	0.1181	0.046*
H12B	0.2639	−0.0105	0.1358	0.046*
O1	0.1997 (7)	0.5145 (7)	0.1604 (5)	0.0747 (17)
H1A	0.1943	0.5830	0.2159	0.090*
H1B	0.2392	0.5803	0.1138	0.090*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0182 (4)	0.0414 (5)	0.0332 (4)	−0.0137 (3)	0.0056 (2)	−0.0064 (3)
N1	0.018 (2)	0.038 (3)	0.034 (2)	−0.0133 (19)	0.0031 (17)	0.0008 (19)
C2	0.021 (3)	0.045 (3)	0.031 (3)	−0.014 (2)	−0.001 (2)	−0.004 (2)
N3	0.021 (2)	0.045 (3)	0.030 (2)	−0.018 (2)	0.0017 (17)	−0.0037 (19)
C4	0.016 (2)	0.026 (3)	0.029 (2)	−0.008 (2)	−0.0010 (18)	0.001 (2)
C5	0.014 (2)	0.030 (3)	0.031 (3)	−0.007 (2)	−0.0001 (18)	0.003 (2)
C6	0.019 (3)	0.037 (3)	0.029 (2)	−0.004 (2)	0.0048 (19)	0.007 (2)
N6	0.030 (3)	0.061 (3)	0.030 (2)	−0.018 (2)	0.0086 (19)	−0.005 (2)
N7	0.021 (2)	0.037 (3)	0.032 (2)	−0.015 (2)	−0.0001 (17)	−0.0038 (18)
C8	0.024 (3)	0.041 (3)	0.037 (3)	−0.011 (2)	0.005 (2)	0.001 (2)
N9	0.015 (2)	0.038 (3)	0.033 (2)	−0.0133 (19)	0.0028 (17)	−0.0002 (18)
N11	0.022 (2)	0.043 (3)	0.032 (2)	−0.016 (2)	0.0040 (18)	−0.0038 (19)
C11	0.021 (3)	0.044 (3)	0.030 (3)	−0.011 (2)	0.005 (2)	−0.004 (2)
C12	0.019 (3)	0.037 (3)	0.032 (3)	−0.004 (2)	0.004 (2)	−0.004 (2)
O11	0.0220 (19)	0.054 (3)	0.0317 (19)	−0.0125 (17)	0.0090 (15)	−0.0059 (17)
O12	0.025 (2)	0.055 (3)	0.038 (2)	−0.0212 (19)	0.0083 (16)	−0.0134 (18)
C21	0.025 (3)	0.039 (3)	0.033 (3)	−0.012 (2)	0.001 (2)	−0.006 (2)
O13	0.038 (2)	0.057 (3)	0.034 (2)	−0.019 (2)	0.0083 (17)	−0.0069 (18)
C22	0.024 (3)	0.049 (4)	0.041 (3)	−0.017 (3)	−0.001 (2)	−0.009 (3)
N12	0.025 (2)	0.044 (3)	0.044 (3)	−0.014 (2)	0.010 (2)	−0.010 (2)
O1	0.043 (3)	0.084 (4)	0.107 (4)	0.012 (3)	0.033 (3)	0.044 (3)

Geometric parameters (Å, °)

Cu1—N11	1.903 (4)	C8—N9	1.330 (7)
Cu1—N9	1.972 (4)	C8—H8	0.9300
Cu1—O11	2.024 (4)	N11—C21	1.310 (7)
Cu1—N12	2.030 (4)	N11—C11	1.451 (6)
Cu1—O1	2.309 (5)	C11—C12	1.513 (7)
N1—C2	1.331 (6)	C11—H11A	0.9700
N1—C6	1.346 (7)	C11—H11B	0.9700
C2—N3	1.337 (6)	C12—O12	1.252 (6)
C2—H2	0.9300	C12—O11	1.276 (6)
N3—C4	1.352 (6)	C21—O13	1.268 (6)
C4—C5	1.369 (6)	C21—C22	1.518 (7)

C4—N9	1.389 (6)	C22—N12	1.479 (7)
C5—N7	1.373 (6)	C22—H22A	0.9700
C5—C6	1.416 (6)	C22—H22B	0.9700
C6—N6	1.339 (6)	N12—H12A	0.8640
N6—H6A	0.8669	N12—H12B	0.8644
N6—H6B	0.8663	O1—H1A	0.8305
N7—C8	1.326 (6)	O1—H1B	0.8219
N7—H7	0.9031		

N11—Cu1—N9	175.42 (19)	C8—N9—Cu1	125.0 (3)
N11—Cu1—O11	82.58 (16)	C4—N9—Cu1	130.4 (3)
N9—Cu1—O11	96.86 (15)	C21—N11—C11	123.2 (4)
N11—Cu1—N12	81.47 (18)	C21—N11—Cu1	119.5 (4)
N9—Cu1—N12	98.07 (17)	C11—N11—Cu1	116.8 (3)
O11—Cu1—N12	159.99 (17)	N11—C11—C12	108.1 (4)
N11—Cu1—O1	93.39 (19)	N11—C11—H11A	110.1
N9—Cu1—O1	91.19 (17)	C12—C11—H11A	110.1
O11—Cu1—O1	94.36 (19)	N11—C11—H11B	110.1
N12—Cu1—O1	98.6 (2)	C12—C11—H11B	110.1
C2—N1—C6	119.2 (4)	H11A—C11—H11B	108.4
N1—C2—N3	128.9 (5)	O12—C12—O11	123.4 (5)
N1—C2—H2	115.6	O12—C12—C11	117.8 (4)
N3—C2—H2	115.6	O11—C12—C11	118.8 (5)
C2—N3—C4	111.7 (4)	C12—O11—Cu1	113.6 (3)
N3—C4—C5	124.6 (4)	O13—C21—N11	127.3 (5)
N3—C4—N9	126.0 (4)	O13—C21—C22	119.7 (5)
C5—C4—N9	109.4 (4)	N11—C21—C22	113.0 (4)
C4—C5—N7	106.5 (4)	N12—C22—C21	109.9 (4)
C4—C5—C6	119.2 (5)	N12—C22—H22A	109.7
N7—C5—C6	134.3 (5)	C21—C22—H22A	109.7
N6—C6—N1	118.7 (5)	N12—C22—H22B	109.7
N6—C6—C5	124.9 (5)	C21—C22—H22B	109.7
N1—C6—C5	116.4 (4)	H22A—C22—H22B	108.2
C6—N6—H6A	128.6	C22—N12—Cu1	107.8 (3)
C6—N6—H6B	123.3	C22—N12—H12A	110.4
H6A—N6—H6B	104.3	Cu1—N12—H12A	116.1
C8—N7—C5	106.7 (4)	C22—N12—H12B	113.6
C8—N7—H7	132.5	Cu1—N12—H12B	105.5
C5—N7—H7	120.8	H12A—N12—H12B	103.5
N7—C8—N9	113.5 (5)	Cu1—O1—H1A	107.6
N7—C8—H8	123.3	Cu1—O1—H1B	121.9
N9—C8—H8	123.3	H1A—O1—H1B	103.0
C8—N9—C4	104.0 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1B···O13^{i}	0.82	2.04	2.740 (6)	143
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Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z$; (iv) $-x+1, -y+1, -z+1$; (v) $-x-1, -y, -z+1$.

Fig. 1

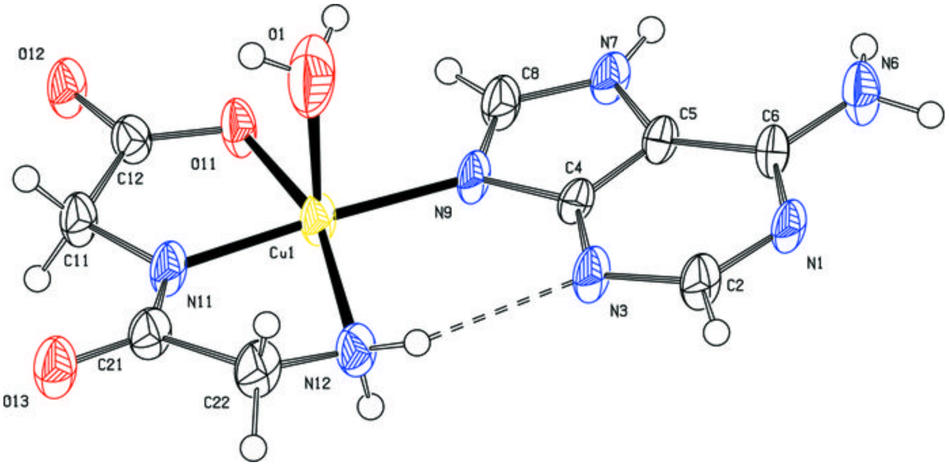
O12
O1
N7
N6
C8
C5
C6
C12
O11
C4
N9
C11
Cu1
N1
N11
N3
C2
C21
N12
O13
C22

Fig. 2