

Bis[1,1-dimethylbiguanide(1-)- κ^2N^2,N^5]copper(II) monohydrate

Li-Ping Lu, Pin Yang, Shi-Dong Qin and Miao-Li Zhu*

Institute of Molecular Science, Chemical Biology and Molecular Engineering
Laboratory of Education Ministry, Shanxi University, Taiyuan, Shanxi 030006,
People's Republic of China

Correspondence e-mail: miaoli@sxu.edu.cn

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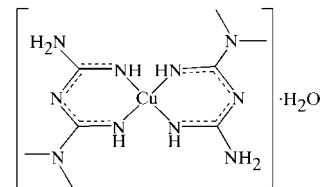
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The crystal structure of the title compound, $[\text{Cu}(\text{C}_4\text{H}_{10}\text{N}_5)_2] \cdot \text{H}_2\text{O}$, contains two independent copper *N,N*-dimethylbiguanide complex units, each with square-planar coordination of the Cu atom by four N atoms. The two complexes have different symmetry, with one Cu atom lying on an inversion centre and the other on a twofold rotation axis. The Cu–N bond lengths are 1.923 (2) and 1.950 (2) Å in the centrosymmetric complex, and 1.928 (2) and 1.938 (2) Å in the non-centrosymmetric complex. The crystal structure is stabilized by N–H···O, O–H···N and N–H···N hydrogen bonds; each water molecule forms four hydrogen bonds involving three different Cu complexes.

Comment

An *N*-substituted derivative of biguanide, *N,N*-dimethylbiguanide, is a powerful oral antihyperglycaemic drug that has

been used in many countries for over 40 years for treating diabetic patients with non-insulin-dependent diabetes mellitus. This compound forms complexes with many metal ions (Ray, 1961; Viossat *et al.*, 1995; Lemoine *et al.*, 1996; Bentefrit *et al.*, 1997; Zhu *et al.*, 2002, 2002a,b). We report here the structure of a new copper(II) complex, (I), of *N,N*-dimethylbiguanide.



(I)

The asymmetric unit of (I) contains two copper *N,N*-dimethylbiguanide complexes and two water molecules (Fig. 1). The metal ions of the copper *N,N*-dimethylbiguanide

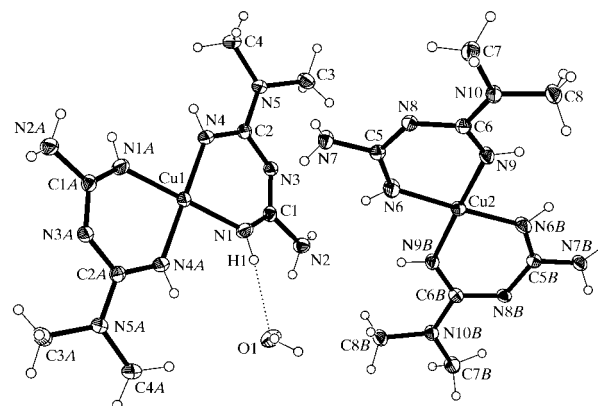


Figure 1

The structure of the title compound, with displacement ellipsoids drawn at the 40% probability level for non-H atoms. [Symmetry codes: (A) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (B) $1 - x, y, \frac{1}{2} - z$.]

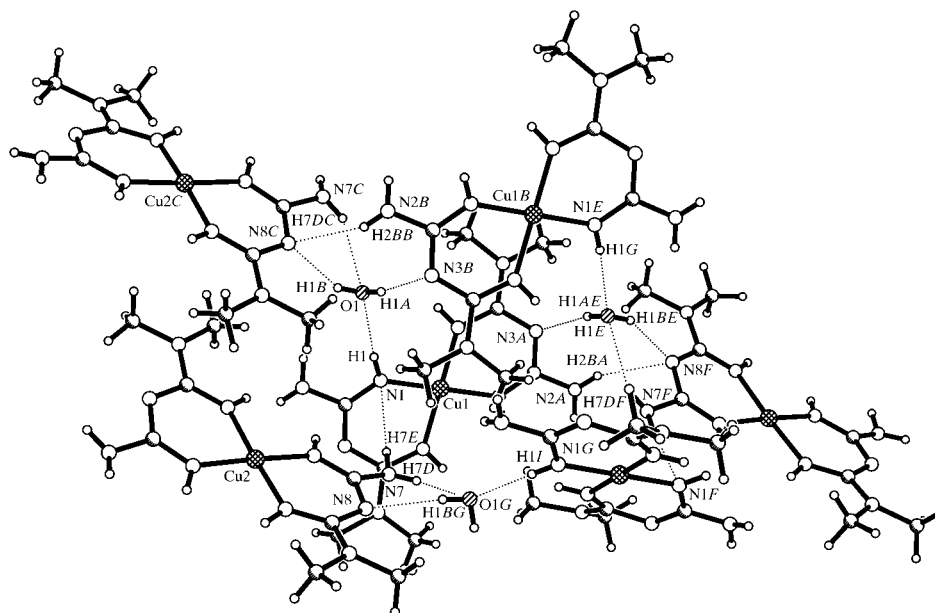


Figure 2

The hydrogen-bond network of the title compound. [Symmetry codes: (A) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (B) $x, y - 1, z$; (C) $x, -y, z - \frac{1}{2}$; (E) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$; (F) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (G) $x, -y, \frac{1}{2} + z$.]

complexes have square-planar coordination, each forming four Cu–N bonds with two bidentate ligands. The two ligands form a slightly distorted plane, with the Cu atom at the centre. The dimethyl groups of the two ligands have a *trans* configuration. These properties agree with those of other copper *N,N*-dimethylbiguanide complexes (Viossat *et al.*, 1995; Lemoine *et al.*, 1996; Zhu *et al.*, 2002*b*). However, in (I), the two copper *N,N*-dimethylbiguanide complex units have different symmetry. Atom Cu1 lies on an inversion centre, while atom Cu2 lies on a twofold rotation axis. The Cu–N bond lengths in the complexes are also slightly different (Table 1).

The crystal structure is stabilized by N–H···O, O–H···N and N–H···N hydrogen bonds (Table 2 and Fig. 2). The water molecule forms four hydrogen bonds involving three different copper *N,N*-dimethylbiguanide complex units, *viz.* two hydrogen bonds with one copper *N,N*-dimethylbiguanide complex (containing atom Cu2) and one hydrogen bond with each of the neighbouring complexes (containing atom Cu1). Each Cu1 complex is connected to a Cu2 complex directly and indirectly *via* N–H···N, N–H···O and O–H···N hydrogen bonds, and neighbouring Cu1 or Cu2 complexes are linked directly by N–H···O and O–H···N hydrogen bonds *via* the water molecules. Antiparallel zigzag [N7–H···O···H–N1···H–]n hydrogen-bond chains run throughout the crystal.

Experimental

All solvents and chemicals were commercially available (reagent grade) and were used without further purification. An aqueous solution of CuCl₂·2H₂O was added dropwise to a 0.1 M KOH solution of *N,N*-dimethylbiguanide, in a 1:1 molar ratio, with stirring. The resulting red–purple solution was filtered and the filtrate was left to stand at room temperature. Red–purple crystals formed after a few days.

Crystal data

[Cu(C ₄ H ₁₀ N ₅) ₂] ₂ ·H ₂ O	<i>D</i> _x = 1.605 Mg m ^{−3}
<i>M</i> _r = 337.90	Mo <i>K</i> α radiation
Monoclinic, <i>C</i> ₂ / <i>c</i>	Cell parameters from 10 688 reflections
<i>a</i> = 30.535 (6) Å	<i>θ</i> = 2.8–27.5°
<i>b</i> = 7.055 (1) Å	<i>μ</i> = 1.58 mm ^{−1}
<i>c</i> = 13.746 (3) Å	<i>T</i> = 173 (2) K
<i>β</i> = 109.18 (3)°	Block, red–purple
<i>V</i> = 2796.9 (10) Å ³	0.45 × 0.20 × 0.15 mm
<i>Z</i> = 8	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	3155 independent reflections
<i>φ</i> and <i>ω</i> scans	2423 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	<i>θ</i> _{max} = 27.5°
<i>T</i> _{min} = 0.537, <i>T</i> _{max} = 0.798	<i>h</i> = 0 → 39
3155 measured reflections	<i>k</i> = 0 → 9
	<i>l</i> = −17 → 16

Table 1

Selected interatomic distances (Å).

Cu1–N1	1.923 (2)	Cu2–N6	1.928 (2)
Cu1–N4	1.950 (2)	Cu2–N9	1.938 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<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···O1	0.85	2.19	3.035 (3)	175
N2–H2B···N8 ⁱ	0.85	2.38	3.193 (3)	160
N7–H7D···O1 ⁱⁱ	0.85	2.24	3.010 (3)	150
N7–H7E···N1	0.85	2.59	3.432 (3)	174
O1–H1A···N3 ⁱⁱⁱ	0.83	2.02	2.838 (3)	167
O1–H1B···N8 ^{iv}	0.79	2.19	2.909 (3)	153

Symmetry codes: (i) *x*, 1 − *y*, *z* − ½; (ii) *x*, −*y*, ½ + *z*; (iii) *x*, *y* − 1, *z*; (iv) *x*, −*y*, *z* − ½.

Refinement

Refinement on <i>F</i> ²	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.040	<i>wR</i> [<i>F</i> ²] = 0.094
<i>S</i> = 0.95	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.05 <i>P</i>) ²]
3155 reflections	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
188 parameters	(Δ/σ) _{max} < 0.001
	Δρ _{max} = 0.66 e Å ^{−3}
	Δρ _{min} = −0.38 e Å ^{−3}

H atoms attached to C atoms were placed in idealized positions, with Csp³–H distances of 0.96 Å, and constrained to ride on their parent atoms, with *U*_{iso}(H) values of 1.5*U*_{eq}(C). H atoms attached to O and N atoms were located from difference Fourier maps (O–H = 0.97 and 0.83 Å, and N–H = 0.85 Å). An overall *U*_{iso} value was refined for the H atoms bonded to N atoms [0.034 (3) Å²]; for the water H atoms, the *U*_{iso} value was set at 0.031 Å².

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1310). Services for accessing these data are described at the back of the journal.

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