

## Bis(1,1-dimethylbiguanido)copper(II) octahydrate

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## Key indicators

Single-crystal X-ray study

$T = 173\text{ K}$

Mean  $\sigma(\text{N}-\text{C}) = 0.002\text{ \AA}$

$R$  factor = 0.026

$wR$  factor = 0.051

Data-to-parameter ratio = 13.8

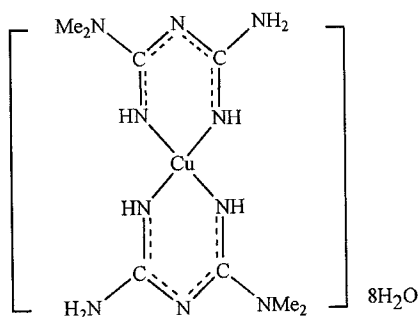
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A complex of a deprotonated form of metformin with  $\text{Cu}^{2+}$ ,  $[\text{Cu}(\text{C}_4\text{H}_{10}\text{N}_5)_2] \cdot 8\text{H}_2\text{O}$ , was prepared from alkaline aqueous solution. The coordination geometry around the Cu atom is square planar, with four N atoms from two bidentate ligands. The deprotonation of the ligand causes an increase in the  $\pi$  conjugation of the C–N–C system, reducing the bond angle at the central N atom to nearly  $120^\circ$ . The dihedral angle between the two six-membered chelate rings in the complex is  $11.31(5)^\circ$ . The Cu atom lies on a twofold rotation axis.

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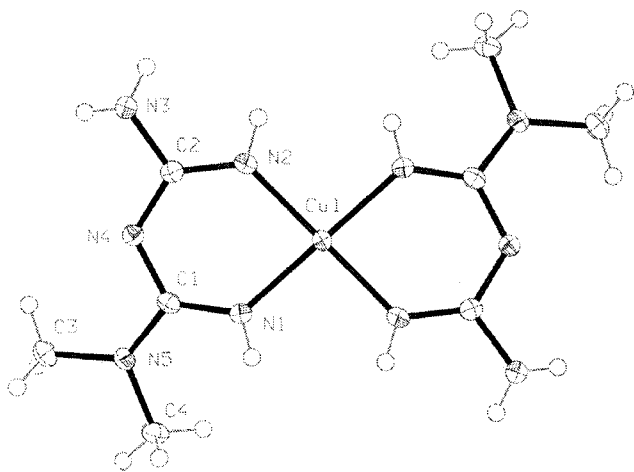
## Comment

Metformin (1,1-dimethylbiguanide) has been introduced as an oral glucose-lowering agent for the treatment of non-insulin dependent diabetes mellitus. Like biguanide, it is a moderately strong base, forming well defined salts and possessing excellent capacity for coordination with transition metals, giving rise to highly colored bidentate chelate complexes. Various metal complexes have been studied, such as  $[\text{PtCl}(\text{C}_4\text{H}_{11}\text{N}_5)(\text{DMSO})]\text{Cl}$  (Viostat *et al.*, 1995),  $[\text{PtCl}_4(\text{C}_4\text{H}_{11}\text{N}_5)(\text{DMSO})]$  (Bentefrit *et al.*, 1997),  $[\text{Co}(\text{C}_4\text{H}_{12}\text{N}_5)\text{Cl}_3]$ ,  $[\text{CuCl}_2(\text{C}_4\text{H}_{11}\text{N}_5)_2]$ ,  $[\text{Cu}(\text{C}_4\text{H}_{11}\text{N}_5)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_5)_2](\text{Cl})(\text{OH})$  (Lemoine *et al.*, 1996), and  $[\text{Zn}(\text{C}_4\text{H}_{12}\text{N}_5)\text{Cl}_3]$  (Zhu, Lu, Jin & Yang, 2002) (DMSO is dimethyl sulfoxide). The metal complexes of biguanide ligands are usually cationic in nature, and their color varies with the nature of the metal ion and its oxidation state, as well as with the number of ligands in the complex. It has been found that the bidentate ligand can chelate to metals in a square-planar configuration through four N atoms of two ligands. Here, we report the synthesis of a red copper complex of a deprotonated form, (I), of metformin (an anionic ligand) and its crystal structure.



(I)

The geometric parameters of (I) are listed in Table 1. The molecular conformation and crystal packing are illustrated in Figs. 1 and 2. The structure can be regarded as a square-planar



**Figure 1**  
A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

coordination of the metal ion through the formation of four  $M-N$  bonds with two bidentate ligands. The central metal atom lies on a crystallographic twofold rotation axis. The two ligands form a slightly distorted plane with the Cu at the center. The dimethyl groups of the two ligands have a *trans* configuration.

The Cu–N bond distances in the structure of (I) are worthy of comment. The values 1.9210 (14) and 1.9428 (13) Å are very similar to those of 1.920 (4) and 1.931 (4) Å in  $[\text{Cu}(\text{C}_4\text{H}_{11}\text{N}_5)_2]\cdot 2\text{HCO}_3$ , and 1.932 (7) and 1.948 (7) Å in  $[\text{Cu}(\text{C}_4\text{H}_{11}\text{N}_5)_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (Viossat *et al.*, 1995; Lemoine *et al.*, 1996). They are significantly longer than the Ni–N bonds in  $[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_5)_2]$  (Zhu, Lu, Yang & Jin, 2002), [1.8478 (17) and

1.8541 (16) Å] and in  $[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_5)_2](\text{Cl})(\text{OH})$  (Lemoine *et al.*, 1996) [1.863 (5) and 1.866 (5) Å]. This large difference is considered to be a result of the removal of an unpaired electron from the  $d(x^2-y^2)$  orbital of the  $d^9$  configuration of  $\text{Cu}^{2+}$  on going to the low-spin  $d^8$  configuration of  $\text{Ni}^{2+}$ , in addition to the small ionic radius difference of  $\text{Ni}^{2+}$  (0.55) and  $\text{Cu}^{2+}$  (0.57) for all coordination numbers (Shannon, 1976).

Another interesting feature in the ligand geometry is the effect of deprotonation. The C–N bond lengths involving the coordinating N atoms of the deprotonated biguanide moiety are 1.3060 (19) and 1.3125 (19) Å. These show delocalization with the C–N4 bonds of 1.3503 (19) and 1.372 (2) Å. Deprotonation of the ligand produces an increase of the  $\pi$  conjugation, reducing the bond angle at N4 to 121.04 (13)°, compared with 124.9 (8)–127.7 (5)° for neutral ligands (Bentefrit *et al.*, 1997; Lemoine *et al.*, 1996).

The dihedral angle between the two chelate rings in (I) is 11.31 (5)°. This is larger than that in  $[\text{Ni}(\text{C}_4\text{H}_{11}\text{N}_5)_2]$  (Zhu, Lu, Yang & Jin, 2002) [0.02 (7)°], and may be due to the larger ionic radius of  $\text{Cu}^{2+}$ . The crystal packing is characterized by 11 intermolecular hydrogen bonds involving N2, N3, and N4 of the metformin as well as all O atoms of solvent water molecules.

## Experimental

1,1-Dimethylbiguanide hydrochloride was purchased from the Wujin Medicine Raw Material Chemical Factory of China.  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  was a commercial sample from Acros, and was used without further purification. An aqueous solution of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  was added dropwise to a 0.1 M KOH solution of the ligand with stirring, in the mole ratio 1:2. The red solution was filtered, and the filtrate was left at room temperature. Red crystals were formed after a few days. The elemental analysis results are in agreement with the structural composition of (I).

### Crystal data

$[\text{Cu}(\text{C}_4\text{H}_{10}\text{N}_5)_2]\cdot 8\text{H}_2\text{O}$   
 $M_r = 464.01$   
 Monoclinic,  $C2/c$   
 $a = 23.561$  (5) Å  
 $b = 6.952$  (1) Å  
 $c = 13.297$  (3) Å  
 $\beta = 105.95$  (3)°  
 $V = 2094.1$  (7) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.472$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 9440 reflections  
 $\theta = 3.1$ –27.5°  
 $\mu = 1.10$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Block, red  
 0.50 × 0.40 × 0.25 mm

### Data collection

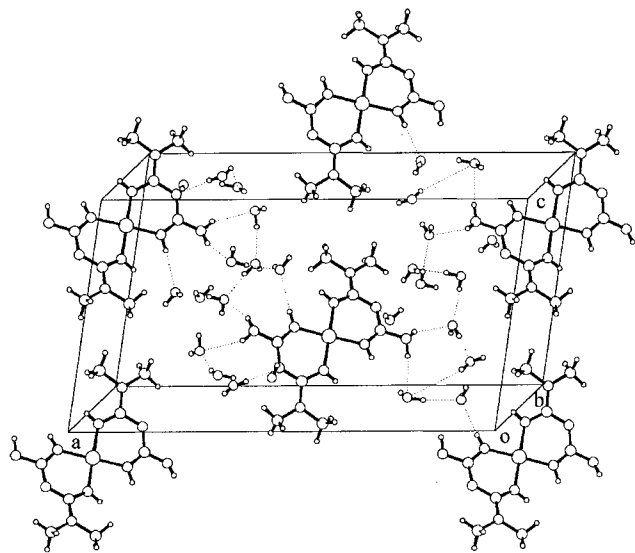
Rigaku RAXIS RAPID IP diffractometer  
 $\varphi$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
 $T_{\min} = 0.596$ ,  $T_{\max} = 0.760$   
 2381 measured reflections

2381 independent reflections  
 1894 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -30 \rightarrow 30$   
 $k = -9 \rightarrow 9$   
 $l = -17 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.051$   
 $S = 0.90$   
 2381 reflections  
 173 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0242P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.008$   
 $\Delta\rho_{\max} = 0.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>



**Figure 2**  
The packing of the title compound, viewed approximately down the  $b$  axis.

**Table 1**  
Selected geometric parameters (Å, °).

Cu1—N2	1.9210 (14)	N3—C2	1.3861 (19)
Cu1—N1	1.9428 (13)	N4—C2	1.3503 (19)
N1—C1	1.3125 (19)	N4—C1	1.372 (2)
N2—C2	1.3060 (19)	N5—C1	1.3647 (19)
N2—Cu1—N1	87.86 (6)	N1—C1—N4	124.15 (14)
C1—N1—Cu1	129.38 (11)	N5—C1—N4	114.63 (13)
C2—N2—Cu1	128.10 (11)	N2—C2—N4	127.96 (13)
C2—N4—C1	121.04 (13)	N2—C2—N3	118.28 (14)
N1—C1—N5	121.22 (14)	N4—C2—N3	113.74 (13)
N2—Cu1—N1—C1	12.15 (15)	C2—N4—C1—N5	−174.39 (14)
N1—Cu1—N2—C2	−2.37 (16)	Cu1—N2—C2—N4	−5.0 (3)
Cu1—N1—C1—N5	164.27 (12)	Cu1—N2—C2—N3	173.56 (12)
Cu1—N1—C1—N4	−15.4 (2)	C1—N4—C2—N2	5.1 (3)
C2—N4—C1—N1	5.3 (2)	C1—N4—C2—N3	−173.49 (14)

**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>
O1—H11A...O2 <sup>j</sup>	0.82 (2)	1.94 (2)	2.737 (2)	165 (2)
O1—H11B...N4	0.82 (2)	2.10 (2)	2.9149 (19)	173 (2)
O2—H12A...N4	0.79 (2)	2.08 (2)	2.8597 (19)	174.3 (19)
O2—H12B...O4 <sup>ii</sup>	0.80 (2)	1.94 (2)	2.727 (2)	167 (2)
O3—H13A...O2 <sup>j</sup>	0.83 (2)	1.95 (2)	2.778 (2)	173 (2)
O3—H13B...N3	0.79 (2)	2.26 (3)	3.049 (2)	177 (2)
O4—H14A...O1 <sup>iii</sup>	0.84 (2)	2.01 (3)	2.834 (2)	169 (3)
O4—H14B...O3 <sup>iv</sup>	0.78 (3)	2.00 (3)	2.764 (2)	166 (2)
N2—H22...O1 <sup>v</sup>	0.849 (17)	2.225 (17)	3.072 (2)	175.5 (15)
N3—H23A...O3 <sup>iii</sup>	0.789 (18)	2.376 (18)	3.103 (2)	153.7 (17)
N3—H23B...O4	0.886 (19)	2.444 (19)	3.272 (2)	155.8 (16)

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

Methyl H atoms were treated as riding, with C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The H atoms on N or O atoms were refined, with  $U_{\text{iso}}(\text{H}) = 0.03 \text{ \AA}^2$  (0.08 for O); N—H distances are in the range 0.81–0.89 Å and the O—H distances are in the range 0.78–0.84 Å.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *MSC/AFD Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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