

Bis{*N'*-[(*E*-amino(imino)methyl]morpholino-carboximidamido}copper(II)

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Key indicators

Single-crystal X-ray study

 $T = 293\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$ R factor = 0.028 wR factor = 0.080

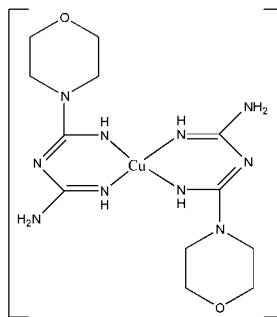
Data-to-parameter ratio = 11.5

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

The title complex of a deprotonated form of morpholine biguanide with Cu^{II} , namely bis(2-morpholinobiguanido)copper(II), $[\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_5\text{O})_2]$, was characterized crystallographically. The Cu^{2+} ion, on a centre of symmetry, is coordinated by four N atoms from two bidentate morpholine biguanide monoanions; the biguanide groups of the two ligands and the copper ion are coplanar. The two morpholine rings of the ligands are in a *trans* configuration and have a chair conformation.

Comment

Biguanide and its *N*-substituted derivatives, acting as *N*-donor monodentate and bidentate ligands, can form complexes with many metal ions (Zhu *et al.*, 2002, 2002*a,b*; Ray, 1961). As the structure of biguanide in solution is pH dependent, its metal complexes are also pH dependent in solution. Different forms of metal complexes with 1,1-dimethylbiguanide anions, cations and neutral molecules have been reported in the literature (Viostat *et al.*, 1995; Lemoine *et al.*, 1996; Zhu *et al.*, 2002; Zhu *et al.*, 2002*a,b*). We report here the crystal structure of a copper complex, (I), of morpholine biguanide.



The geometric parameters of (I) are listed in Table 1. The molecular structure and crystal packing are illustrated in Figs. 1 and 2. The Cu^{2+} ion lies on a centre of symmetry and is coordinated by four N atoms from two bidentate morpholine biguanide monoanions. The biguanide groups of the two ligands and the copper ion define a plane with an r.m.s. deviation of 0.112 \AA , and a maximum deviation of 0.209 (2) \AA for N4. In free morpholine biguanide, metformin and *N*-phenethylbiguanide, the two guanidium units are not coplanar (Handa & Saha, 1973; Zhu *et al.*, 2003*a,b*). The Cu–N bond lengths are 1.911 (2) and 1.944 (2) \AA , similar to those in copper(II) metformin complexes (Viostat *et al.*, 1995; Lemoine *et al.*, 1996; Zhu *et al.*, 2002*b*), but slightly shorter than those (2.001–2.031 \AA) in other copper complex of planar ligands, such as phenanthroline (Lu *et al.*, 2003). Most of the C–N bonds (C1–N3, C2–N3, C2–N4 and C2–N5) are longer, but C1–N1 is shorter and C1–N2 does not change

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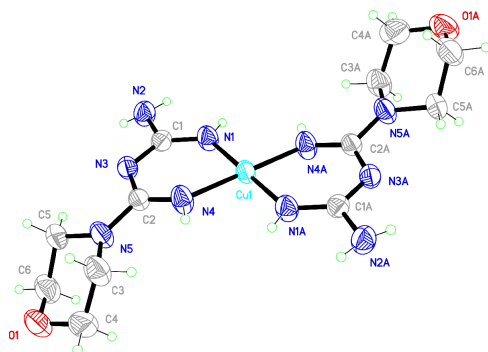


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. The suffix *A* denotes an inversion-related atom (symmetry code: $1 - x, -y, -z$).

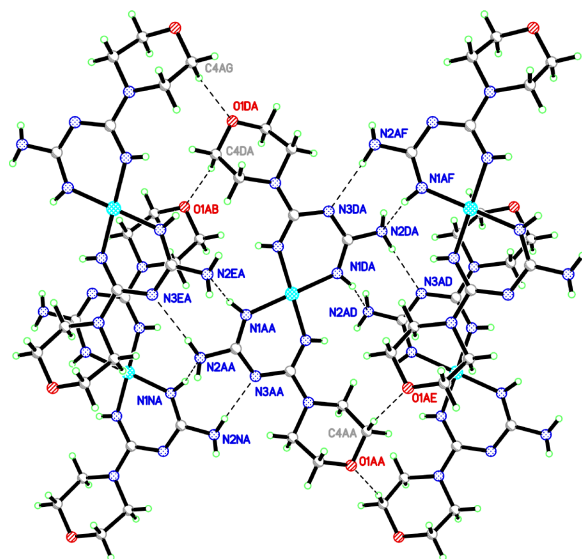


Figure 2
The molecular packing, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

much, compared to free morpholine biguanide (Handa & Saha, 1973). The two morpholine rings of the ligands are in a *trans* configuration, and have a chair conformation.

In the crystal packing, the molecules are held together by a number of intermolecular hydrogen bonds involving atoms N1, N2 and N3 (Table 2).

Experimental

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 a 1:2 molar ratio. The red solution was filtered, and the filtrate was left at room temperature. Red crystals of the title complex formed after a few days.

Crystal data

$[\text{Cu}(\text{C}_6\text{H}_{12}\text{N}_5\text{O})_2]$
 $M_r = 403.95$
Monoclinic, $P2_1/c$
 $a = 9.185(2) \text{ \AA}$
 $b = 12.681(3) \text{ \AA}$
 $c = 7.7791(17) \text{ \AA}$
 $\beta = 110.579(3)^\circ$
 $V = 848.2(3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.582 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2289 reflections
 $\theta = 2.9\text{--}26.7^\circ$
 $\mu = 1.32 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Block, red
 $0.40 \times 0.40 \times 0.30 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.602$, $T_{\max} = 0.672$
3429 measured reflections

1501 independent reflections
1290 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$
 $\theta_{\max} = 25.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -15 \rightarrow 14$
 $l = -9 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.080$
 $S = 1.01$
1501 reflections
131 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0541P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	1.9107 (17)	C1—N2	1.370 (3)
Cu1—N4	1.9437 (18)	O1—C6	1.415 (3)
N1—C1	1.312 (3)	O1—C4	1.416 (4)
N4—C2	1.311 (3)	C2—N5	1.367 (3)
N3—C1	1.339 (3)	N5—C5	1.453 (3)
N3—C2	1.348 (2)	N5—C3	1.463 (3)
N1—Cu1—N4	87.74 (8)	C6—O1—C4	108.79 (17)
C1—N1—Cu1	128.21 (14)	N4—C2—N3	125.0 (2)
C2—N4—Cu1	127.74 (17)	N4—C2—N5	121.26 (19)
C1—N3—C2	120.80 (18)	N3—C2—N5	113.69 (19)
N1—C1—N3	127.72 (18)	C2—N5—C5	122.34 (19)
N1—C1—N2	118.31 (18)	C2—N5—C3	125.51 (18)
N3—C1—N2	113.96 (18)	C5—N5—C3	111.37 (17)
N4—Cu1—N1—C1	−4.11 (19)	C2—N3—C1—N2	179.99 (19)
N1—Cu1—N4—C2	15.3 (2)	Cu1—N4—C2—N3	−22.7 (3)
Cu1—N1—C1—N3	−1.3 (3)	Cu1—N4—C2—N5	156.06 (18)
Cu1—N1—C1—N2	177.28 (15)	C1—N3—C2—N4	13.8 (3)
C2—N3—C1—N1	−1.4 (3)	C1—N3—C2—N5	−165.08 (19)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
$\text{N2—H2A}\cdots\text{N3}^i$	0.89 (2)	2.39 (3)	3.274 (3)	178 (2)
$\text{N1—H1}\cdots\text{N2}^i$	0.86 (2)	2.53 (2)	3.284 (3)	146.8 (19)

Symmetry code: (i) $x, -\frac{1}{2} - y, z - \frac{1}{2}$.

H atoms attached to C atoms were placed in geometrically idealized positions, with $\text{C—H} = 0.97 \text{ \AA}$, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms attached to N atoms were located in a difference Fourier map and refined isotropically.

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

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