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Bis(biguanido-κ^2N,N')copper(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(N–C) = 0.004 Å
R factor = 0.040
wR factor = 0.096
Data-to-parameter ratio = 11.4

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

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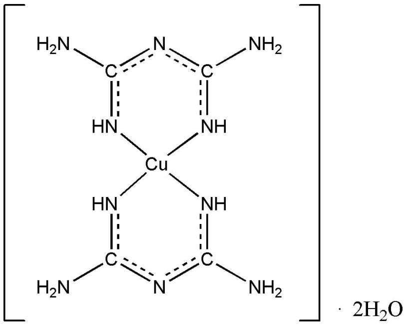
In the title compound, $[Cu(C_2H_6N_5)_2]\cdot 2H_2O$, the Cu^{2+} cation, lying at a centre of symmetry, is coordinated by four N atoms from two bidenate ligands, forming a square-planar complex. The deprotonation of the ligand causes an increase in π-conjugation. Hydrogen bonds between solvent water and the complex help to stabilize the three-dimensional network structure.

Comment

Biguanide and its derivatives are important in coordination and pharmaceutical chemistry (Ray, 1961). Biguanide has an excellent capacity for coordination with transition metals, giving rise to highly coloured bidentate chelate complexes and influencing their pharmaceutical properties (Zhu, Lu & Yang, 2004). Many protonated and neutral forms of biguanide compounds have been studied, such as $[PtCl_4(C_4H_{11}N_5)(DMSO)]$ (DMSO is dimethyl sulfoxide; Bentefrit *et al.*, 1997), $[Co(C_4H_{12}N_5)Cl_3]$ (Lemoine *et al.*, 1996), $[Zn(C_4H_{12}N_5)Cl_3]$ (Zhu *et al.*, 2002), $[Tl(C_4H_{12}N_5)Br_4]$ (He *et al.*, 2002), $C_4H_{12}N_5NO_3$ (Zhu, Lu & Yang, 2003), $(C_{10}H_{17}N_5)[ZnCl_4]$ (Zhu, Yang & Lu, 2003), $(C_2H_9N_5)[Mn(C_2H_7N_5)_3](NO_3)_6$ (Lu, Zhu & Yang, 2004), $C_4H_{12}N_5Br$ (Lu, Zhang, Feng & Zhu, 2004*b*), and $C_4H_{13}N_5C_2O_4\cdot H_2O$ and $C_4H_{13}N_5SO_4\cdot H_2O$ (Lu, Zhang, Feng & Zhu, 2004*a*). Deprotonated ligands coordinated to Ni^{2+} and Cu^{2+} have also been reported recently (Zhu, Lu, Yang & Jin, 2002*a*,*b*; Lu & Zhu, 2003; Lu, Yang *et al.*, 2004). Here, we describe the crystal structure of the title compound, (I).



(I)

Selected geometric parameters of (I) are listed in Table 1, and the molecular structure is illustrated in Fig. 1. Atom Cu1 lies on a crystallographic centre of symmetry and is coordinated by four N atoms of the two bidentate ligands in a square-planar form. The coordination characteristics of (I) are very similar to those of $[Ni(C_4H_{10}N_5)_2]$ and $[Cu(C_4H_{10}N_5)_2]\cdot 8H_2O$ (Zhu, Lu, Yang & Jin, 2002*a*,*b*), $[Cu(C_6H_{12}N_5O)_2]$ (Lu & Zhu, 2003), and $[Cu(C_4H_{10}N_5)_2]\cdot H_2O$ (Lu, Yang *et al.*,

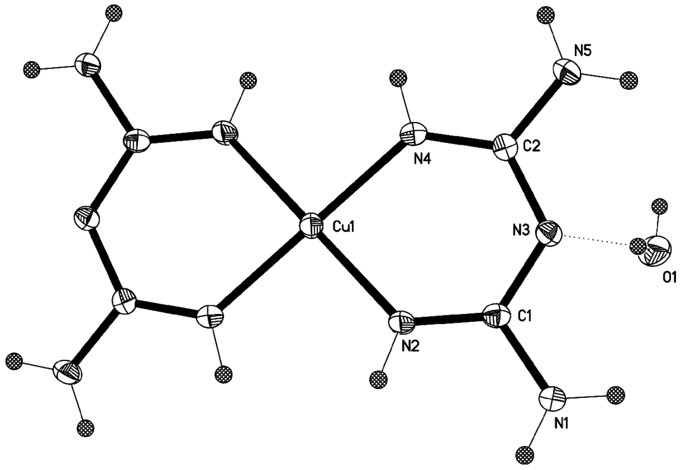


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry operator $(1 - x, -y, 1 - z)$. The dashed line indicates a hydrogen bond.

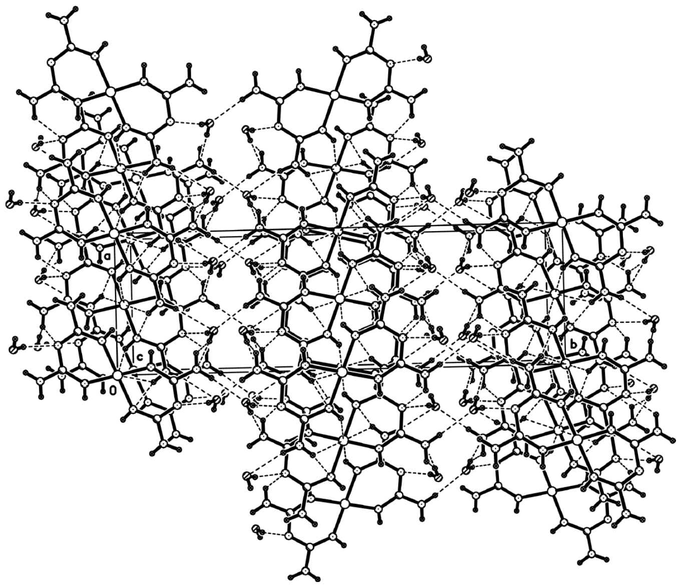


Figure 2
The packing of the title compound, viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

2004). From Table 1, we note that all C—N bonds display a certain degree of delocalization. Thus, the deprotonation of the ligand produces an increase of π-conjugation in the biguanide group compared with its protonated and neutral forms.

Hydrogen bonds between the solvent water and the complex help to stabilize the three-dimensional network structure (Table 2 and Fig. 2).

Experimental

Chemicals of reagent grade were used without further purification. $CuSO_4{\cdot}5H_2O$ in aqueous solution was added dropwise, with constant stirring, to a 0.1 *M* KOH solution containing biguanidium sulfate (1:2 molar ratio). Filtration gave a rose-red solution. The filtrate was left to stand at room temperature and, after a few days, rose-red crystals of the title complex were formed.

Crystal data

$[Cu(C_2H_6N_5)_2]{\cdot}2H_2O$
$M_r = 299.81$
Orthorhombic, *Pbca*
$a = 7.133$ (3) Å
$b = 22.536$ (8) Å
$c = 7.056$ (3) Å
$V = 1134.2$ (8) Å^3
$Z = 4$
$D_x = 1.756$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1978 reflections
$\theta = 3.4$–$26.6°$
$\mu = 1.94$ mm^{-1}
$T = 298$ (2) K
Block, rose-red
$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.576$, $T_{max} = 0.677$
4926 measured reflections

1001 independent reflections
908 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 25.0°$
$h = -8 \rightarrow 3$
$k = -26 \rightarrow 26$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.096$
$S = 1.20$
1001 reflections
88 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.3149P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.039 (3)

Table 1
Selected geometric parameters (Å, °).

C1—N2	1.316 (4)	C2—N5	1.350 (4)
C1—N3	1.352 (4)	C2—N3	1.357 (4)
C1—N1	1.370 (4)	Cu1—N2	1.927 (3)
C2—N4	1.323 (4)	Cu1—N4	1.954 (3)
N2—C1—N3	126.8 (3)	N4—C2—N3	126.0 (3)
N2—C1—N1	119.4 (3)	N5—C2—N3	113.4 (3)
N3—C1—N1	113.7 (3)	N2—Cu1—N4	87.86 (12)
N4—C2—N5	120.6 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H12···N1^{i}	0.77 (5)	2.28 (5)	3.046 (5)	173 (5)
O1—H11···N3	0.77 (4)	2.22 (5)	2.972 (4)	166 (4)
N5—H5*B*···O1^{i}	0.86	2.31	3.094 (4)	151
N1—H1*B*···O1^{ii}	0.86	2.13	2.975 (4)	166

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

N-bound H atoms were placed in geometrically idealized positions with N—H = 0.86 Å and refined as riding with $U_{iso}(H) = 1.2U_{eq}(N)$. H atoms attached to O were located in a difference Fourier map and refined freely.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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