

Bis(1,1-dimethylbiguanido)nickel(II)

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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{N}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.030

wR factor = 0.072

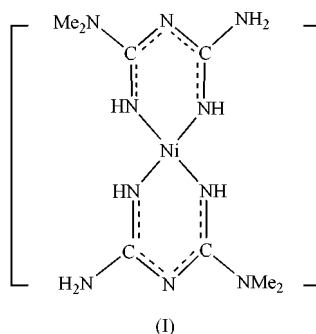
Data-to-parameter ratio = 14.4

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

The title compound, $[\text{Ni}(\text{C}_4\text{H}_{10}\text{N}_5)_2]$, was prepared from an aqueous KOH solution. The coordination geometry around the Ni atom is planar, with the central metal bonded to four ligand N atoms in two bidentate ligands. The deprotonation of the ligand causes an increase of the π -conjugation in the C–N–C system, reducing the bond angle at the N atom to $118.46(16)^\circ$.

Comment

Biguanide and its *N*-substituted derivatives are pharmacologically useful agents for the treatment of hyperglycaemia (Charles & Eschwege, 1999), malaria (Jensen *et al.*, 2001), influenza (Denys *et al.*, 1977), bacteria (Rosin *et al.*, 2001) and tumours (Bentefrit *et al.*, 1997). The structure of biguanide in solution is pH-dependent because of the strong basic character of the polar guanidine moiety. This results in its metal complexes also being pH-dependent in solution. Like biguanide, metformin (1,1-dimethylbiguanide, MET) exists in various forms: diprotonated $(\text{H}_2\text{MET})^{2+}$ in strong acidic solution, monoprotonated $(\text{HMET})^+$ in weak acid, MET in neutral and deprotonated $(\text{MET})^-$ in strong alkali solution (Fig. 1). Complexes in species $(\text{H}_2\text{MET})^{2+}$, $(\text{HMET})^+$, and MET with metal ions have been reported (Lemoine *et al.*, 1996; Zhu *et al.*, 2002). However, the synthesis and structure of the complex of MET^- with Ni^{2+} differ significantly from those of these other complexes. In the light of this, the title complex, (I), has been prepared and its crystal structure is presented here.



The geometric parameters of (I) are listed in Table 1. The molecular structure is illustrated in Fig. 2. In brief, the structure can be viewed as square-planar, with the metal ion in the centre bonded to two bidentate ligands. The complex is centrosymmetric, with the central metal atom on a crystallographic centre of symmetry. The ligands are not completely planar. The two methyl groups of the two ligands are in a *trans*-configuration.

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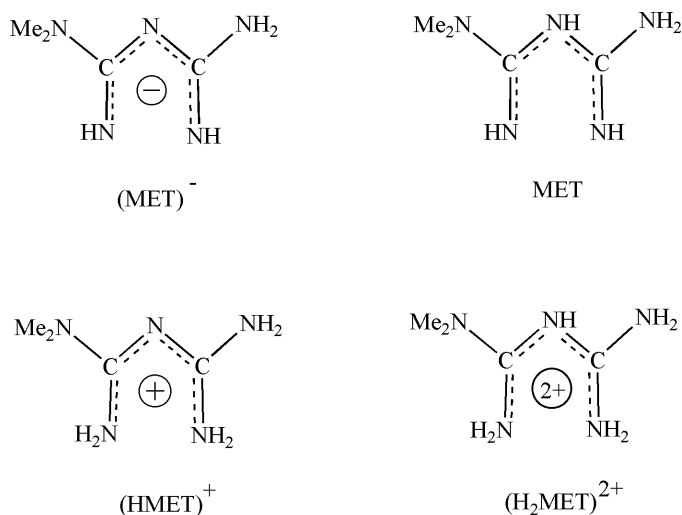


Figure 1
The forms of 1,1-dimethylbiguanide in solution at different pH values.

In (I), the Ni–N bond distances, with values of 1.8480 (17) and 1.8543 (16) Å, are just a little shorter than those of 1.863 (5) and 1.866 (5) Å in $[\text{Ni}(\text{MET})_2](\text{Cl})(\text{OH})$ (Lemoine *et al.*, 1996). The interaction of Ni^{2+} with the biguanide ligand in the deprotonated form is slightly stronger than the other species. Deprotonation leads to significant changes in the geometry of the ligand. From Table 1, we note that the C1–N1 and C2–N2 bond lengths are 1.314 (2) and 1.324 (2) Å, displaying a certain degree of delocalization. A similar conclusion can be drawn for the C–N4 bonds, with lengths of 1.341 (2) and 1.354 (2) Å. The delocalization of the C–N(ring) is smaller than that of the C–N(ligand). In addition, deprotonation of the ligand produces an increase of the π -

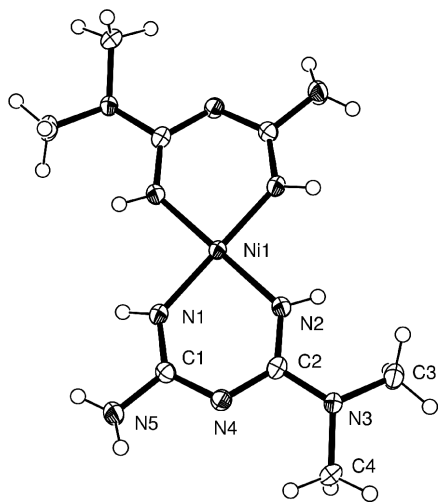


Figure 2
A view of the molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

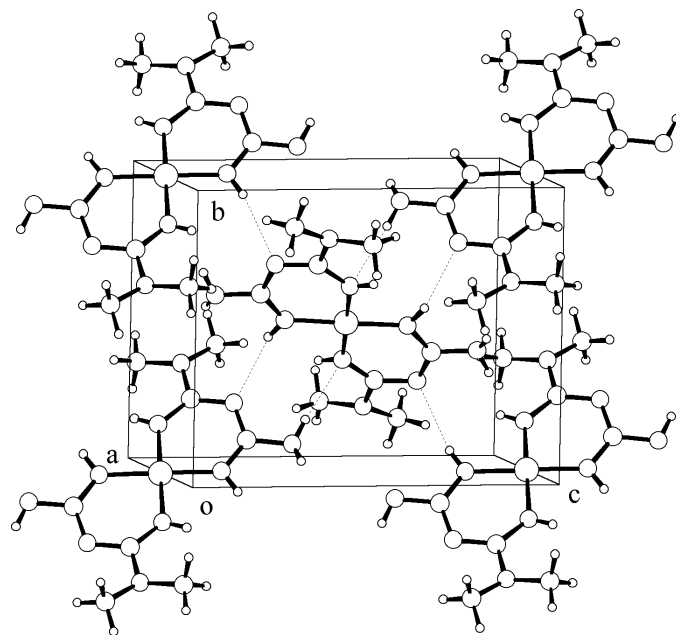


Figure 3
A packing diagram of the title complex.

conjugation in the central C–N–C system, reducing the bond angle at the N atom to 118.47 (16)°. In other species this angle ranges from 124.9 (8) to 127.7 (5)° (Bentefrit *et al.*, 1997; Lemoine *et al.*, 1996).

Experimental

1,1-Dimethylbiguanide hydrochloride was purchased from the Wujin Medicine Raw Material Chemical Factory of China, m.p. 495.5 K. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was obtained commercially from Across without further purification. Crystal of (I) were grown from an aqueous KOH solution of the ligand and metal chloride as follows: a solution of metal chloride was added dropwise to 0.1 M KOH solution (in the ratio 1:2), with stirring. The orange solution was filtered, the filtrate was left at room temperature and orange crystals grew at the bottom of the flask after 3 d. The results of the elemental analysis are completely in agreement with the structural composition of (I).

Crystal data

$[\text{Ni}(\text{C}_4\text{H}_{10}\text{N}_5)_2]$
 $M_r = 315.05$
Monoclinic, $P2_1/c$
 $a = 6.412$ (1) Å
 $b = 9.032$ (2) Å
 $c = 11.239$ (2) Å
 $\beta = 97.05$ (3)°
 $V = 646.0$ (2) Å³
 $Z = 2$

$D_x = 1.620$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1564 reflections
 $\theta = 2.9$ – 27.5 °
 $\mu = 1.51$ mm⁻¹
 $T = 173$ (2) K
Block, orange
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku R-Axis RAPID IP diffractometer
 φ scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.540$, $T_{\max} = 0.740$
1564 measured reflections

1494 independent reflections
1159 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 27.5$ °
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 11$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.072$
 $S = 1.03$
 1467 reflections
 102 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Ni1—N1	1.8480 (17)	N3—C3	1.457 (2)
Ni1—N2	1.8543 (16)	N3—C4	1.463 (3)
N1—C1	1.314 (2)	N4—C2	1.341 (2)
N2—C2	1.324 (2)	N4—C1	1.354 (2)
N3—C2	1.383 (2)	N5—C1	1.372 (2)
N1—Ni1—N2	88.82 (7)	N1—C1—N4	127.12 (17)
C1—N1—Ni1	128.60 (13)	N1—C1—N5	119.47 (18)
C2—N2—Ni1	129.70 (14)	N4—C1—N5	113.32 (17)
C2—N3—C3	118.05 (17)	N2—C2—N4	125.66 (17)
C2—N3—C4	119.55 (16)	N2—C2—N3	119.64 (17)
C3—N3—C4	113.65 (17)	N4—C2—N3	114.63 (17)
C2—N4—C1	118.46 (16)		
N2 ⁱ —Ni1—N1—C1	-168.71 (17)	C2—N4—C1—N1	-7.0 (3)
N2—Ni1—N1—C1	11.29 (17)	C2—N4—C1—N5	169.45 (17)
N1 ⁱ —Ni1—N2—C2	172.91 (18)	Ni1—N2—C2—N4	-2.8 (3)
N1—Ni1—N2—C2	-7.09 (18)	Ni1—N2—C2—N3	-179.43 (14)
N1 ⁱ —Ni1—N2—C2	172.91 (18)	C1—N4—C2—N2	11.5 (3)
Ni1—N1—C1—N4	-6.5 (3)	C1—N4—C2—N3	-171.65 (16)
Ni1—N1—C1—N5	177.29 (14)		

Symmetry code: (i) $1 - x, -y, -z$.

Table 2
 Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N5—H15A \cdots N2 ⁱ	0.86 (3)	2.43 (3)	3.269 (3)	164 (3)
N1—H11 \cdots N4 ⁱⁱ	0.83 (3)	2.31 (4)	3.100 (2)	159 (3)

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

H atoms attached to C were treated as riding, with C—H = 0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$ of the parent atom. In addition, the methyl groups were allowed to rotate, but not to tip. The coordinates of the H atoms bonded to N were refined with $U_{\text{iso}}(\text{H}) = 0.08 \text{ \AA}^2$.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *SHELXS97* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS97*; 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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