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N-Phenethylbiguanidium tetrachlorozincate(II)

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The title compound, $(C_{10}H_{17}N_5)[ZnCl_4]$, was crystallized from an aqueous solution (pH 2) containing a 1:1 molar ratio of $ZnCl_2$ and 1-phenethylbiguanide hydrochloride. The geometry of the tetrachlorozincate(II) anion is a slightly distorted tetrahedron. The *N*-phenethylbiguanidium divalent cation is diprotonated at the two imino groups, resulting in an intramolecular N—H···N hydrogen bond, which stabilizes the conformation of the cation in the structure. The dihedral angle between the two guanidine groups is 48.7 (2)°.

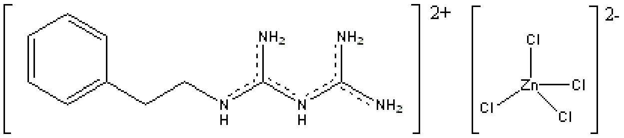
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.063
Data-to-parameter ratio = 15.0

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

Comment

Phenformin (1-phenethylbiguanide hydrochloride) is a synthetic oral hypoglycemic agent used to control maturity-onset diabetes. Pharmacologically, phenformin acts to enhance anaerobic glycolysis, decrease gluconeogenesis, and inhibit intestinal absorption of glucose. As studies have shown that phenformin has two negative side effects, lactic acidosis and shorter lifespans for patients taking phenformin, its use has decreased significantly (University Diabetes Program Research Group, 1975). In some countries, such as the US and most European countries, phenformin has been entirely withdrawn from the market. Most people now use metformin (1,1-dimethylbiguanide hydrochloride) when a biguanide is to be used. However, phenformin itself is still available in developing countries (Kwong & Brubacher, 1998; Haupt & Panten, 1997). Zinc also has many biological functions. It is considered to be an essential nutrient that is required for optimal growth and normal development of vertebrate organisms, as well as being important for maintaining the structure of many proteins. From previous research results, it has been known for many years that zinc mimics the actions of insulin on cells, including promotion of both lipogenesis and glucose transport. Zinc deficiency may indeed affect the optimal functioning of the insulin-signaling pathway (Tang & Shay, 2001; Lynch *et al.*, 2001 Coulston & Dandona, 1980; May & Contoreggi, 1982).



(I)

Our current research is aimed at preparing the zinc(II) complex of *N*-phenethylbiguanide, similar to another biguanide complex (Zhu, Lu, Yang & Jin, 2002), in order to analyse the role of metal ions on antidiabetes agents, because the monoprotonated, neutral and deprotonated molecules of the biguanides can function as mono- and bidentate ligands to

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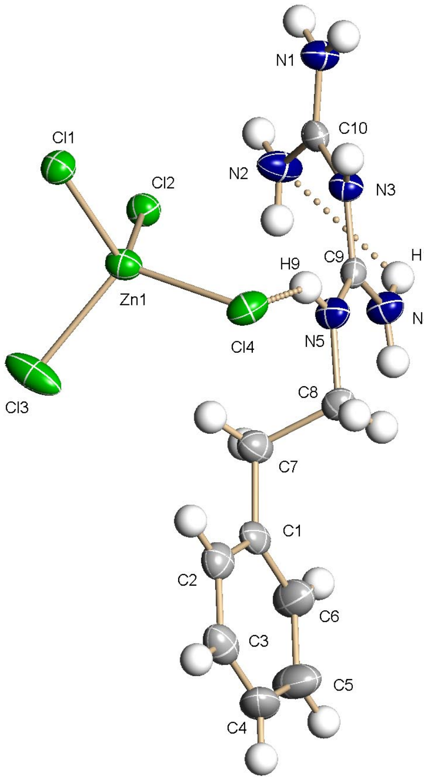

Figure 1
A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii. The dotted line represents a hydrogen bond.

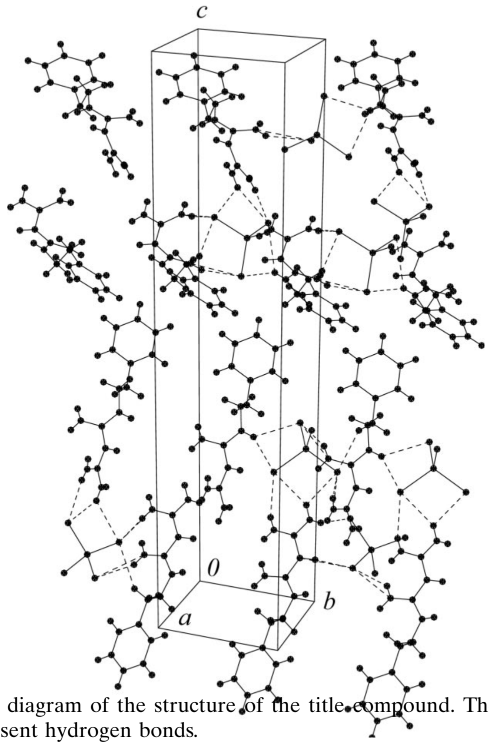

Figure 2
A packing diagram of the structure of the title compound. The dashed lines represent hydrogen bonds.

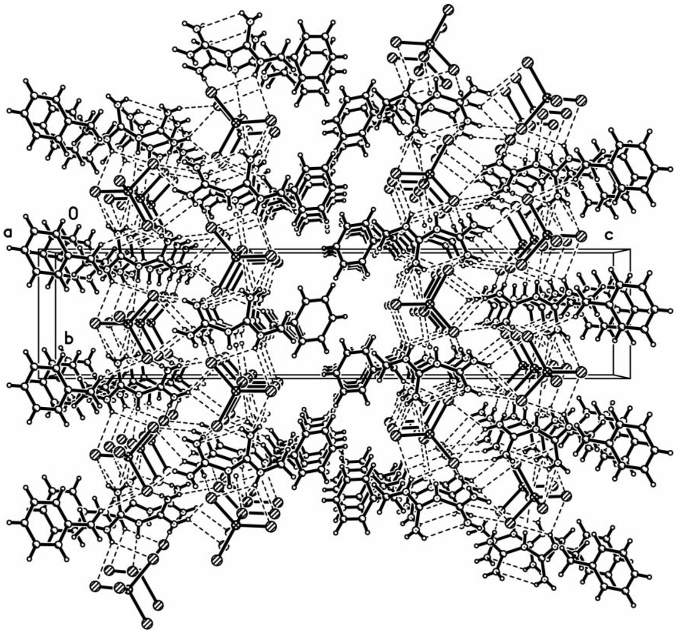

Figure 3
Projection of the crystal structure of (I) along the *a* axis. The dashed lines represent hydrogen bonds.

form complexes with Zn^{II}, Cu^{II} and Ni^{II} (Zhu, Lu, Jin & Yang, 2002; Zhu, Lu, Yang & Jin, 2002*a*,*b*). However, in this case, the *N*-phenethylbiguanidium did not act as a mono- or bidentate ligand to form the desired complex. Instead, the reaction produced a diprotonated divalent cation that formed a salt by cocrystallizing, at low pH, with a $ZnCl_4^{2-}$ anion. Interestingly, we note that this is the first diprotonated *N*-phenethylbiguanide to be studied in the solid state. The structures of two polymorphs of the chloride salt of the monoprotonated form have been reported (Herrnstadt *et al.*, 1979; Soriano-Lesh *et al.*, 1998). In these monprotonated salts, there are two independent *N*-phenethylbiguanidinium cations in the asymmetric unit that form hydrogen-bonded dimers.

Selected geometric parameters are listed in Table 1, and a perspective view of the structure is shown in Fig. 1. In the title complex, (I), the sites of diprotonation (at the two imino groups) and the conformation of the cation are different from monoprotonated (at the terminal imino group) biguanide derivatives, such as $(C_4H_{12}N_5)[ZnCl_3]$ (Zhu, Lu, Yang & Jin, 2002), $(C_6H_{14}N_5O)[ZnCl_3]$ (Yang & Zhu, 1991, 1992), $C_{10}H_{16}N_5^+\cdot Cl^-$ (Herrnstadt *et al.*, 1979; Soriano-Lesh *et al.*, 1998), $(C_4H_{12}N_5)[TlBr_4]$ (He *et al.*, 2002), and $C_4H_{12}N_5^+\cdot Cl^-$ (Hariharan *et al.*, 1989). All the C—N bond distances in (I) are shorter than single bonds and longer than double bonds, indicating a delocalization of π-electron density across the biguanide group. In addition, the molecules in the crystal are held together by a number of intermolecular N—H···Cl interactions (Desiraju, 1991). A weak N—H···N intramolecular hydrogen bond stabilizes the cation conformation (Fig. 1). Hydrogen-bond parameters are listed in Table 2, and a packing diagram and a projection of the crystal structure are shown in Figs. 2 and 3, respectively.

In the structure of (I), atom N3 is a bridging N atom linking the two guanidine groups of the cation. The C9—N3—C10 angle [127.2 (3)°] is larger than those found in the other biguanide derivatives listed in Table 3. As a result of protonation, there is a notable difference in the interplanar angle between the two guanidine groups in mono- and diprotonated residues. Thus the dihedral angle in compound (I) is smaller than those in the monoprotonated biguanides and obviously larger than that of bidentate chelated forms. The central angle of the C—N—C chain in (I) is the largest of all the biguanidines listed in Table 3.

Experimental

Crystals of (I) were grown from an aqueous solution, at pH 2, of zinc(II) dichloride dihydrate (1.0 mmol) and *N*-phenethylbiguanide hydrochloride (1.0 mmol). The solution was left at room temperature and crystals formed after one to three months. The elemental analysis result was in agreement with the structural composition of (I).

Crystal data

$(C_{10}H_{17}N_5)[ZnCl_4]$
$M_r = 414.46$
Orthorhombic, $P2_12_12_1$
$a = 6.6088$ (10) Å
$b = 7.5837$ (12) Å
$c = 34.710$ (5) Å
$V = 1739.6$ (5) Å^3
$Z = 4$
$D_x = 1.582$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4240 reflections
$\theta = 2.8$–26.4°
$\mu = 2.02$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.40 × 0.40 × 0.30 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min} = 0.467$, $T_{\max} = 0.545$
7460 measured reflections

3197 independent reflections
3064 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25.5°$
$h = -7 \rightarrow 8$
$k = -9 \rightarrow 6$
$l = -42 \rightarrow 35$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.063$
$S = 1.04$
3197 reflections
213 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Absolute structure: Flack (1983); 1291 Friedel pairs
Flack parameter = 0.010 (12)

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.2487 (9)	C9—N4	1.319 (4)
Zn1—Cl4	2.2492 (9)	C9—N3	1.382 (4)
Zn1—Cl3	2.2686 (10)	C10—N1	1.298 (4)
Zn1—Cl2	2.2894 (9)	C10—N2	1.303 (4)
C8—N5	1.463 (4)	C10—N3	1.359 (4)
C9—N5	1.292 (4)		
Cl1—Zn1—Cl4	114.14 (3)	N5—C9—N3	117.3 (3)
Cl1—Zn1—Cl3	106.09 (4)	N4—C9—N3	118.7 (3)
Cl4—Zn1—Cl3	110.00 (4)	N1—C10—N2	121.5 (3)
Cl1—Zn1—Cl2	108.42 (3)	N1—C10—N3	117.0 (3)
Cl4—Zn1—Cl2	109.68 (3)	N2—C10—N3	121.4 (3)
Cl3—Zn1—Cl2	108.30 (4)	C10—N3—C9	127.2 (3)
N5—C9—N4	123.9 (3)	C9—N5—C8	126.8 (3)
N1—C10—N3—C9	−175.0 (3)	N4—C9—N3—C10	45.7 (5)
N2—C10—N3—C9	7.8 (5)	N4—C9—N5—C8	−1.2 (5)
N5—C9—N3—C10	−137.8 (3)	N3—C9—N5—C8	−177.5 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H16···Cl1$^{\rm i}$	0.89 (4)	2.73 (4)	3.319 (3)	125 (3)
N1—H16···Cl2$^{\rm i}$	0.89 (4)	2.68 (4)	3.471 (4)	148 (3)
N3—H12···Cl3$^{\rm ii}$	0.88 (4)	2.21 (4)	3.088 (3)	173 (3)
N4—H11···Cl4$^{\rm iii}$	0.84 (5)	2.44 (5)	3.219 (3)	155 (4)
N1—H15···Cl2$^{\rm ii}$	0.77 (3)	2.60 (3)	3.319 (3)	156 (3)
N5—H9···Cl2	0.77 (3)	2.89 (3)	3.433 (3)	130 (3)
N5—H9···Cl4	0.77 (3)	2.77 (3)	3.374 (3)	137 (3)
N2—H14···Cl2$^{\rm i}$	0.74 (3)	2.63 (3)	3.330 (4)	160 (3)
N2—H13···Cl1$^{\rm iii}$	0.88 (4)	2.37 (4)	3.237 (3)	170 (3)
N4—H10···N2	0.80 (4)	2.63 (3)	2.960 (5)	106 (3)

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

Table 3
Relationship of guanidine planes in biguanide (Å, °).

Compound	Plane 1 C(N1/N2/N3)	Plane 2 C′(N3/N4/N5)	Dihedral angle between planes	C—N—C′ (centre)
a	0.024 (3)	−0.019 (3)	48.7 (2)	127.2 (3)
b	0.042 (2)	−0.030 (2)	67.5 (1)	118.7 (1)
c	−0.008 (15)	−0.039 (15)	62.3 (5)	124.9 (11)
d			77.6 (2)	119.1 (3)
e			67.9 (1)	122.5 (3)
f			54.8 (1)	123.1 (2)
			72.5 (1)	123.8 (2)
g	0.002 (2)	−0.011 (3)	9.7 (1)	121.0 (1)
h	0.021 (2)	−0.024 (2)	9.8 (2)	118.5 (2)
i			48.4	126.2 (3)
j	0.017	0.010	58.9	122.7

Notes: (*a*) $(C_{10}H_{17}N_5)[ZnCl_4]$ (this work); (*b*) $[ZnCl_3(C_4H_{12}N_5)]$ (Zhu *et al.*, 2002); (*c*) $(C_4H_{12}N_5)[TlBr_4]$ (He *et al.*, 2002); (*d*) $[ZnCl_3(C_6H_{14}N_5O)]$ (Yang & Zhu, 1991, 1992); (*e*) $C_4H_{11}N_5\cdot HCl$ (Hariharan *et al.*, 1989); (*f*) dimer of $C_{10}H_{15}N_5\cdot HCl$ (Soriano-Lesh *et al.*, 1998); (*g*) $[Cu(C_4H_{10}N_5)_2]\cdot 8H_2O$ (Zhu *et al.*, 2002*a*); (*h*) $[Ni(C_4H_{10}N_5)_2]$ (Zhu *et al.*, 2002*b*); (*i*) $C_2H_9N_5^{2+}\cdot SO_4^{2-}\cdot H_2O$ (Brown, 1967); (*j*) $C_{11}H_{16}ClN_5\cdot HCl$ (Pinkerton & Schwarzenbach, 1978).

H atoms attached to C atoms were placed in geometrically idealized positions, with Csp^2—H = 0.99 Å and Csp^3—H = 0.95 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms on N atoms were located in difference Fourier maps and refined with $U_{\rm iso} = 0.01$–0.08 Å^2 and N—H distances in the range 0.74–0.89 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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