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# (*N*-{Amino[(diaminomethylidene)amino]methylidene}-*N*-methylmethanaminium)tribromidozinc(II)

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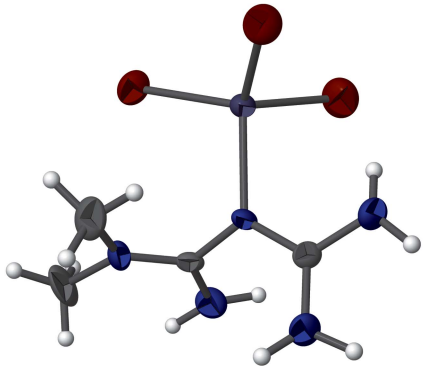
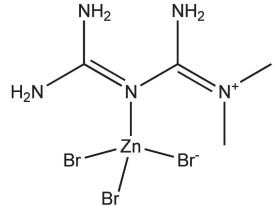
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title compound, $[ZnBr_3(C_4H_{12}N_5)]$, the $Zn^{II}$ cation is tetrahedrally coordinated by three bromide ions and the (*N*-{amino[(diaminomethylene)amino]methylene}-*N*-methylmethanaminium) cation that binds through the central N atom. The complex is of interest as a potential antidiabetic drug of the biguanide family. The crystal structure is stabilized by an extensive series of N—H···Br and C—H···Br hydrogen bonds, which combine to form a three-dimensional structure.

**3D view**



**Chemical scheme**




## Structure description

The title compound is a complex with a ligand derived from hypoglycaemic agent Metformin, *N*,*N*-dimethylimidodicarbonimidic diamide. This has potential applications as an oral antidiabetic drug of the biguanide family (Welton, 1999; Pérez-Fernández *et al.*, 2013). The asymmetric unit (Fig. 1) consists of a zinc(II) metal atom, tetrahedrally coordinated to the (*N*-{amino[(diaminomethylene)amino]methylene}-*N*-methylmethanaminium) cation (MetforminH+) and three bromide ions. A rearrangement of the protonated Metformin molecule results in the N2 atom carrying a positive charge and the MetforminH+ ligand binds through atom N1. Bond lengths and angles (Table 1) confirm a tetrahedral coordination environment for the zinc(II) atom. The MetforminH+ ligand has two planar segments, N1—C4—N4—N5 and N1—C1—N3—N2—C2—C3 inclined to one another at an angle of 65.5 (9)°.

In the crystal structure, N3—H3*F*···Br1 and N5—H5*G*···Br3 hydrogen bonds, Table 2, form an $R_2^2(10)$ motif while the N3—H3*F*···Br1 and N3—H3*G*···Br1 contacts generate $R_4^2(8)$ rings. Atoms Br2 and Br3 act as bifurcated acceptors, forming N5—H5*F*···Br2 and

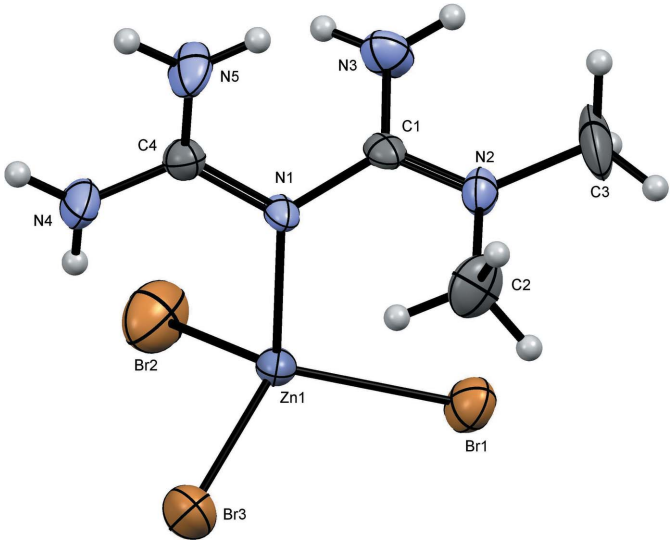



**Figure 1**
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary size.

C3—H3*C*···Br2 together with N4—H4*G*···Br3 and N5—H5*G*···Br3 hydrogen bonds that enclose $R_2^1(8)$ and $R_2^1(6)$ rings, respectively. These numerous interactions combine to produce an infinite three-dimensional network structure (Fig. 2).

## Synthesis and crystallization

A mixture of $ZnBr_2$ (100 mg, 0.44 mmol) and MetforminH+ hydrochloride (73.61 mg, 0.44 mmol) in 20 ml of an ethanol/water (1:1) solvent mixture was refluxed for 3 h. The resulting solution was evaporated using a rotary evaporator affording a microcrystalline white solid powder that was washed with 20 ml cold ethanol and dried under vacuum to produce the title product in a 52.76% yield, m.p. 170–172°C. CHN analysis: found C: 12.90%; H: 3.17%; N: 17.70%. Calculated, C: 12.29%; H: 3.10%; N: 17.92%. Crystals suitable for analysis by X-ray diffraction were grown from a saturated ethanol solution of the title compound at 4°C.

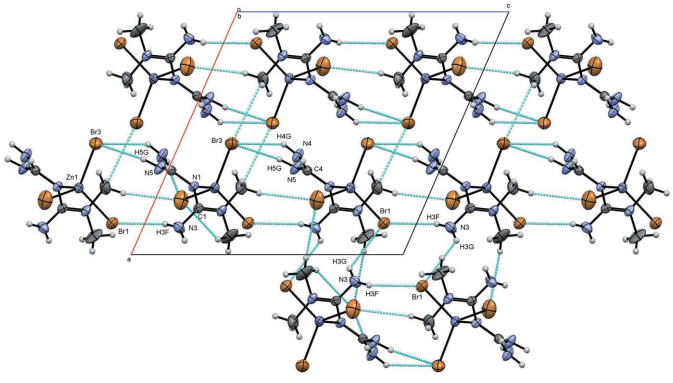


**Figure 2**
Part of the crystal packing of the title compound showing N—H···Br hydrogen bonds forming the $R_2^2(10)$, $R_4^2(8)$ and $R_2^1(6)$ ring motifs.

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

| | | | |
|---|---|---|---|
| Br1—Zn1 | 2.3659 (12) | Br3—Zn1 | 2.3461 (14) |
| Br2—Zn1 | 2.3499 (15) | N1—Zn1 | 2.077 (6) |
| | | | |
| N1—Zn1—Br1 | 107.40 (17) | Br3—Zn1—Br1 | 116.16 (5) |
| N1—Zn1—Br2 | 103.87 (19) | Br2—Zn1—Br1 | 110.13 (6) |
| N1—Zn1—Br3 | 106.84 (19) | Br3—Zn1—Br2 | 111.57 (6) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*F*···Br1$^{i}$ | 0.91 (2) | 2.67 (5) | 3.500 (8) | 152 (8) |
| N3—H3*G*···Br1$^{ii}$ | 0.91 (2) | 2.85 (8) | 3.416 (7) | 122 (7) |
| C3—H3*D*···Br2$^{ii}$ | 0.96 | 3.04 | 3.959 (13) | 160 |
| C3—H3*C*···Br2$^{iii}$ | 0.96 | 2.98 | 3.665 (12) | 130 |
| C2—H2*A*···Br2$^{iv}$ | 0.96 | 2.84 | 3.747 (10) | 157 |
| N5—H5*G*···Br3$^{i}$ | 0.91 (2) | 2.68 (5) | 3.526 (7) | 155 (8) |
| N4—H4*G*···Br3$^{i}$ | 0.92 (2) | 2.65 (6) | 3.446 (7) | 146 (8) |

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y+1, z$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[ZnBr_3(C_4H_{12}N_5)]$ |
| $M_r$ | 435.29 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 298 |
| $a, b, c$ (Å) | 12.8934 (9), 7.6576 (4), 13.2374 (9) |
| $\beta$ (°) | 113.580 (8) |
| $V$ (Å$^3$) | 1197.83 (15) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 12.03 |
| Crystal size (mm) | 0.26 × 0.23 × 0.15 |
| | |
| Data collection | |
| Diffractometer | Agilent Xcalibur Atlas Gemini |
| Absorption correction | Analytical (*CrysAlis RED*; Agilent, 2013) |
| $T_{min}$, $T_{max}$ | 0.094, 0.215 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 11024, 2985, 2312 |
| $R_{int}$ | 0.032 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.693 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.062, 0.206, 1.08 |
| No. of reflections | 2985 |
| No. of parameters | 138 |
| No. of restraints | 6 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 2.95, −2.33 |

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS2014* (Sheldrick, 2008), *SHELXS2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *WinGX* (Farrugia, 2012).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

## Acknowledgements

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# full crystallographic data

*IUCrData* (2016). **1**, x160855 [doi:10.1107/S2414314616008555]

## (*N*-{Amino[(diaminomethylidene)amino]methylidene}-*N*-methylmethanaminium)tribromidozinc(II)

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**(*N*-{Amino[(diaminomethylidene)amino]methylidene}-*N*-methylmethanaminium)tribromidozinc(II)**

*Crystal data*

$[ZnBr_3(C_4H_{12}N_5)]$
$M_r$ = 435.29
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a$ = 12.8934 (9) Å
$b$ = 7.6576 (4) Å
$c$ = 13.2374 (9) Å
$\beta$ = 113.580 (8)°
$V$ = 1197.83 (15) Å$^3$
$Z$ = 4
$F(000)$ = 824
$D_x$ = 2.414 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 3360 reflections
$\theta$ = 3.5–29.5°
$\mu$ = 12.03 mm$^{-1}$
$T$ = 298 K
Block, colourless
0.26 × 0.23 × 0.15 mm

*Data collection*

Agilent Xcalibur Atlas Gemini diffractometer
Graphite monochromator
Detector resolution: 10.4685 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: analytical (*CrysAlis RED*; Agilent, 2013)
$T_{min}$ = 0.094, $T_{max}$ = 0.215
11024 measured reflections
2985 independent reflections
2312 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032
$\theta_{max}$ = 29.5°, $\theta_{min}$ = 3.5°
$h$ = −17→16
$k$ = −10→10
$l$ = −15→17

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.206
$S$ = 1.08
2985 reflections
138 parameters
6 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1109P)^2 + 10.4971P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.95 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.33 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. PROBLEM: Check Calcd Positive Residual Density on Zn1 3.07 eA3 RESPONSE: Residual close to Br1 (0.6 A), possible consequence of an unresolved disorder.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.8091 (6) | 0.9864 (9) | 0.6725 (6) | 0.0231 (14) |
| C2 | 0.7232 (9) | 1.0786 (14) | 0.7966 (8) | 0.044 (2) |
| H2A | 0.7472 | 1.0422 | 0.872 | 0.067* |
| H2B | 0.6625 | 1.0051 | 0.7504 | 0.067* |
| H2C | 0.6977 | 1.1975 | 0.7894 | 0.067* |
| C3 | 0.9242 (10) | 1.1520 (14) | 0.8330 (9) | 0.056 (3) |
| H3C | 0.9363 | 1.2516 | 0.795 | 0.085* |
| H3D | 0.9864 | 1.0723 | 0.8501 | 0.085* |
| H3E | 0.9189 | 1.1893 | 0.9 | 0.085* |
| C4 | 0.6535 (7) | 0.9019 (10) | 0.5127 (6) | 0.0259 (15) |
| Br1 | 0.87048 (8) | 0.66446 (14) | 0.87937 (7) | 0.0410 (3) |
| Br2 | 0.77575 (13) | 0.43610 (16) | 0.59611 (10) | 0.0639 (4) |
| Br3 | 0.54231 (9) | 0.58951 (16) | 0.69159 (8) | 0.0485 (3) |
| N1 | 0.7192 (5) | 0.8762 (8) | 0.6202 (5) | 0.0225 (12) |
| N2 | 0.8191 (6) | 1.0647 (9) | 0.7628 (5) | 0.0279 (14) |
| N3 | 0.8886 (7) | 0.9994 (10) | 0.6327 (7) | 0.0356 (16) |
| N4 | 0.5913 (7) | 0.7710 (11) | 0.4543 (6) | 0.0398 (18) |
| N5 | 0.6419 (7) | 1.0577 (10) | 0.4666 (6) | 0.0375 (17) |
| Zn1 | 0.72516 (8) | 0.64108 (11) | 0.70055 (7) | 0.0245 (3) |
| H3F | 0.874 (8) | 0.923 (10) | 0.576 (5) | 0.029* |
| H3G | 0.942 (6) | 1.076 (10) | 0.674 (6) | 0.029* |
| H5F | 0.645 (8) | 1.163 (6) | 0.500 (7) | 0.029* |
| H5G | 0.606 (7) | 1.055 (13) | 0.3919 (19) | 0.029* |
| H4F | 0.617 (8) | 0.663 (6) | 0.483 (7) | 0.029* |
| H4G | 0.547 (7) | 0.808 (12) | 0.385 (3) | 0.029* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.025 (3) | 0.017 (3) | 0.025 (3) | −0.001 (3) | 0.008 (3) | 0.006 (3) |
| C2 | 0.055 (6) | 0.045 (5) | 0.040 (5) | 0.008 (5) | 0.025 (5) | −0.012 (4) |
| C3 | 0.055 (6) | 0.040 (5) | 0.045 (6) | −0.017 (5) | −0.010 (5) | −0.015 (4) |
| C4 | 0.025 (4) | 0.027 (4) | 0.025 (4) | −0.001 (3) | 0.010 (3) | 0.002 (3) |
| Br1 | 0.0369 (5) | 0.0498 (6) | 0.0317 (5) | 0.0027 (4) | 0.0088 (4) | 0.0037 (4) |
| Br2 | 0.0919 (10) | 0.0437 (6) | 0.0574 (7) | 0.0084 (6) | 0.0312 (7) | −0.0042 (5) |
| Br3 | 0.0416 (6) | 0.0593 (7) | 0.0437 (6) | −0.0129 (5) | 0.0161 (4) | −0.0027 (5) |
| N1 | 0.026 (3) | 0.016 (3) | 0.021 (3) | −0.005 (2) | 0.004 (2) | 0.003 (2) |
| N2 | 0.032 (3) | 0.024 (3) | 0.022 (3) | −0.003 (3) | 0.005 (3) | −0.005 (3) |
| N3 | 0.034 (4) | 0.037 (4) | 0.043 (4) | −0.006 (3) | 0.022 (3) | −0.005 (3) |
| N4 | 0.048 (4) | 0.039 (4) | 0.021 (3) | −0.009 (4) | 0.003 (3) | 0.002 (3) |
| N5 | 0.047 (4) | 0.030 (4) | 0.024 (3) | 0.004 (3) | 0.002 (3) | 0.006 (3) |
| Zn1 | 0.0285 (5) | 0.0213 (4) | 0.0225 (4) | −0.0033 (3) | 0.0089 (4) | 0.0012 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—N2 | 1.297 (10) | C4—N4 | 1.322 (11) |
| C1—N3 | 1.330 (10) | C4—N1 | 1.348 (10) |
| C1—N1 | 1.376 (9) | Br1—Zn1 | 2.3659 (12) |
| C2—N2 | 1.477 (12) | Br2—Zn1 | 2.3499 (15) |
| C2—H2A | 0.96 | Br3—Zn1 | 2.3461 (14) |
| C2—H2B | 0.96 | N1—Zn1 | 2.077 (6) |
| C2—H2C | 0.96 | N3—H3F | 0.91 (2) |
| C3—N2 | 1.463 (11) | N3—H3G | 0.91 (2) |
| C3—H3C | 0.96 | N4—H4F | 0.91 (2) |
| C3—H3D | 0.96 | N4—H4G | 0.92 (2) |
| C3—H3E | 0.96 | N5—H5F | 0.91 (2) |
| C4—N5 | 1.322 (11) | N5—H5G | 0.91 (2) |
| | | | |
| N2—C1—N3 | 121.5 (7) | C1—N1—Zn1 | 115.0 (5) |
| N2—C1—N1 | 120.0 (7) | C1—N2—C3 | 121.5 (8) |
| N3—C1—N1 | 118.3 (7) | C1—N2—C2 | 121.7 (7) |
| N2—C2—H2A | 109.5 | C3—N2—C2 | 116.7 (8) |
| N2—C2—H2B | 109.5 | C1—N3—H3F | 110 (6) |
| H2A—C2—H2B | 109.5 | C1—N3—H3G | 110 (6) |
| N2—C2—H2C | 109.5 | H3F—N3—H3G | 140 (9) |
| H2A—C2—H2C | 109.5 | C4—N4—H4F | 114 (6) |
| H2B—C2—H2C | 109.5 | C4—N4—H4G | 110 (6) |
| N2—C3—H3C | 109.5 | H4F—N4—H4G | 133 (9) |
| N2—C3—H3D | 109.5 | C4—N5—H5F | 127 (6) |
| H3C—C3—H3D | 109.5 | C4—N5—H5G | 113 (6) |
| N2—C3—H3E | 109.5 | H5F—N5—H5G | 117 (9) |
| H3C—C3—H3E | 109.5 | N1—Zn1—Br1 | 107.40 (17) |
| H3D—C3—H3E | 109.5 | N1—Zn1—Br2 | 103.87 (19) |
| N5—C4—N4 | 119.0 (7) | N1—Zn1—Br3 | 106.84 (19) |
| N5—C4—N1 | 121.7 (7) | Br3—Zn1—Br1 | 116.16 (5) |
| N4—C4—N1 | 119.0 (7) | Br2—Zn1—Br1 | 110.13 (6) |
| C4—N1—C1 | 119.3 (6) | Br3—Zn1—Br2 | 111.57 (6) |
| C4—N1—Zn1 | 123.1 (5) | | |
| | | | |
| N5—C4—N1—C1 | −26.7 (12) | N2—C1—N1—Zn1 | −71.2 (8) |
| N4—C4—N1—C1 | 159.3 (8) | N3—C1—N1—Zn1 | 103.8 (7) |
| N5—C4—N1—Zn1 | 172.5 (6) | N3—C1—N2—C3 | −8.1 (12) |
| N4—C4—N1—Zn1 | −1.5 (11) | N1—C1—N2—C3 | 166.7 (8) |
| N2—C1—N1—C4 | 126.5 (8) | N3—C1—N2—C2 | 168.4 (8) |
| N3—C1—N1—C4 | −58.5 (10) | N1—C1—N2—C2 | −16.8 (11) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3*F*···Br1$^{i}$ | 0.91 (2) | 2.67 (5) | 3.500 (8) | 152 (8) |
| N3—H3*G*···Br1$^{ii}$ | 0.91 (2) | 2.85 (8) | 3.416 (7) | 122 (7) |

| | | | | |
|---|---|---|---|---|
| C3—H3*D*···Br2$^{ii}$ | 0.96 | 3.04 | 3.959 (13) | 160 |
| C3—H3*C*···Br2$^{iii}$ | 0.96 | 2.98 | 3.665 (12) | 130 |
| C2—H2*A*···Br2$^{iv}$ | 0.96 | 2.84 | 3.747 (10) | 157 |
| N5—H5*G*···Br3$^{i}$ | 0.91 (2) | 2.68 (5) | 3.526 (7) | 155 (8) |
| N4—H4*G*···Br3$^{i}$ | 0.92 (2) | 2.65 (6) | 3.446 (7) | 146 (8) |

Symmetry codes: (i) $x$, $-y+3/2$, $z-1/2$; (ii) $-x+2$, $y+1/2$, $-z+3/2$; (iii) $x$, $y+1$, $z$; (iv) $x$, $-y+3/2$, $z+1/2$.