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Crystal structure of bis{2-[amino(iminiumyl)methyl]-1,1-dimethylguanidine} carbonate methanol disolvate

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In the title solvated molecular salt, $2C_4H_{12}N_5^+\cdot CO_3^{2-}\cdot 2CH_3OH$, the complete carbonate ion is generated by crystallographic twofold symmetry, with the C atom and one O atom lying on the rotation axis. The cation is twisted about the central C—N bond [C—N—C—N = −137.7 (6)°]. In the crystal, the components are linked by N—H···O, N—H···N and O—H···O hydrogen bonds, generating a three-dimensional supramolecular network.

Keywords: crystal structure; metformin; sodium carbonate; hydrogen bonding.

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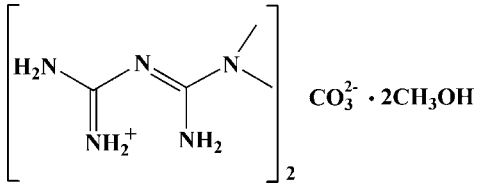
1. Related literature

For background to and medical applications of metformin (systematic name: *N*,*N*-dimethylimidodicarbonimidic diamide), see: Castagnolo *et al.* (2011); De Jager *et al.* (2005); Pérez-Fernández *et al.* (2013); Yardımcı & Özaltın (2005); Xi *et al.* (2008); Li *et al.* (2005). For a related structure, see: Huang *et al.* (2008).



2. Experimental

2.1. Crystal data

$2C_4H_{12}N_5^+\cdot CO_3^{2-}\cdot 2CH_4O$ M_r = 384.46

Monoclinic, $C2/c$
a = 13.5726 (12) Å
b = 10.5634 (8) Å
c = 13.9825 (13) Å
β = 90.386 (1)°
V = 2004.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 K
0.40 × 0.32 × 0.29 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.961, T_{max} = 0.971
4837 measured reflections
1749 independent reflections
947 reflections with $I > 2\sigma(I)$
R_{int} = 0.065

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.083
$wR(F^2)$ = 0.280
S = 1.02
1749 reflections
123 parameters
6 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.86	2.04	2.883 (5)	166
N1—H1B···N3^{ii}	0.86	2.21	3.069 (6)	175
N2—H2A···O1^{iii}	0.86	1.96	2.818 (5)	178
N2—H2B···O3^{iv}	0.86	2.08	2.896 (6)	159
N5—H5A···O1^{iv}	0.86	1.95	2.728 (4)	150
O3—H3···O2	0.82	1.77	2.591 (5)	177

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

Data collection: *APEX2* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7495).

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Crystal structure of bis{2-[amino(iminiumyl)methyl]-1,1-dimethylguanidine} carbonate methanol disolvate

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S1. Structural commentary

Metformin, an oral antidiabetic drug, has been extensively used throughout the world over the last five decades to treat type-2 diabetes mellitus[Castagnolo *et al.* , 2011; De Jager *et al.* , 2005; Pérez-Fernández *et al.* , 2013], in particular, in overweight and obese people. Metformin has a distinct advantage of lowering serum glucose levels without causing hyper-insulinemia and subsequent risk of hypoglycemia [Yardimci *et al.* , 2005; Xi *et al.* , 2008; Liu *et al.* , 2005]. In order to find a substance that enhances the therapeutic effects of metformin, and exhibits additional pancreas-protecting effects, we synthesized the title compound (Fig. 1). Some examples of related structures already appear in the literature[Pérez-Fernández *et al.* , 2013; Huamg *et al.* , 2008]. The structure of the title compound contains two metformin molecules, one methanol molecule and carbonate ion (Fig. 1). In the crystal, N—H···O, N—H···N and O—H···O hydrogen bonds connect molecules to form a two-dimensional network parallel to (001) (Fig. 2).

S2. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 1.The N—H hydrogen atom was located in a difference Fourier map and freely refined: N—H = 0.86 Å. The C-bound H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.96 Å with U_{iso} (H) = 1.2 or 1.5U_{eq} (C).

S3. Synthesis and crystallization

A methanol solution (20 ml) of sodium carbonate (485 mg, 3.03 mmol) and metformin hydrochloride (500 mg, 3.03 mmol) was stirred for 12 h at room temperature. The solid part (sodium chloride) was filtered off. The rest of the solution was slowly evaporated at room temperature, yielding colourless blocks of the title compound.

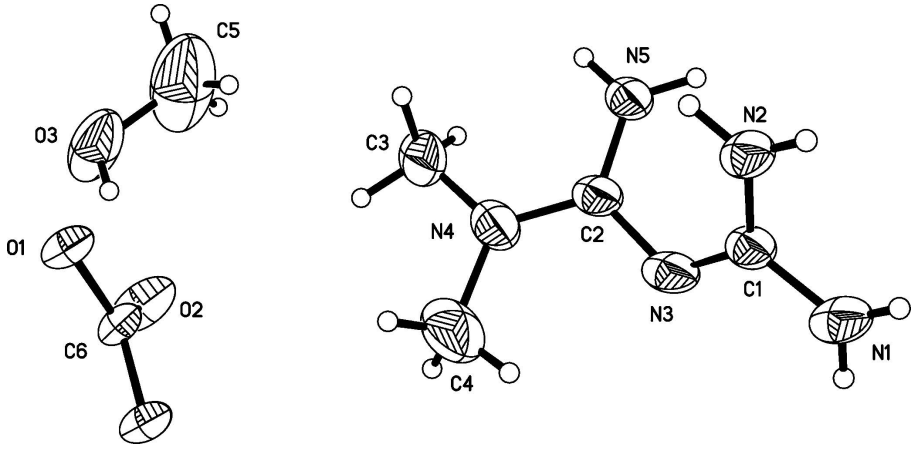

Figure 1

The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

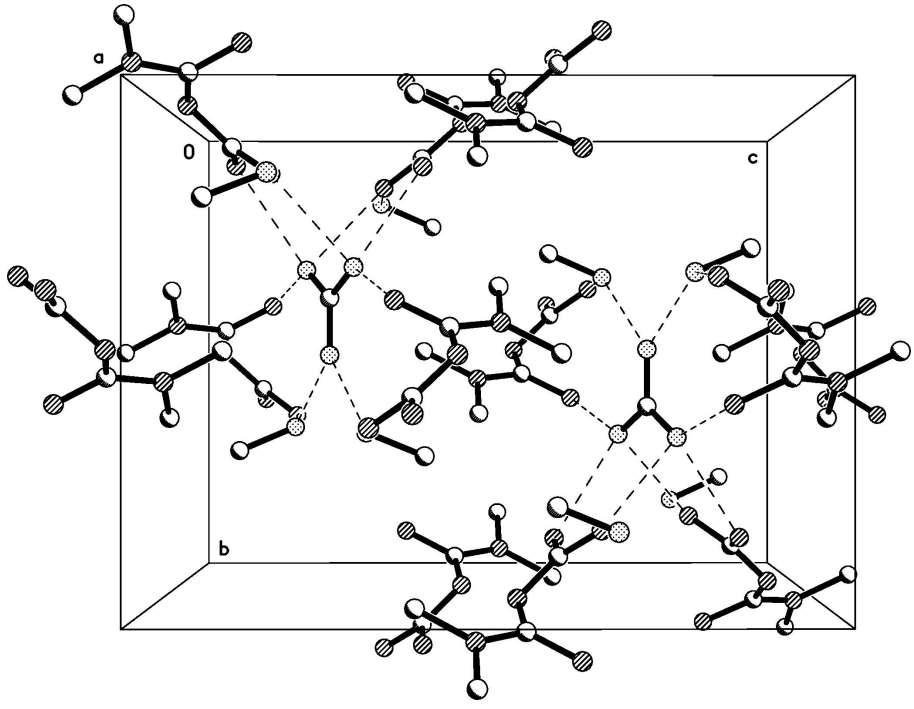

Figure 2

Part of the crystal structure with the hydrogen bonds drawn as dashed lines.

Bis{2-[amino(iminiumyl)methyl]-1,1-dimethylguanidine} carbonate methanol disolvate

Crystal data

$2C_4H_{12}N_5^+\cdot CO_3^{2-}\cdot 2CH_4O$
M_r = 384.46
Monoclinic, *C*2/*c*
a = 13.5726 (12) Å
b = 10.5634 (8) Å
c = 13.9825 (13) Å
β = 90.386 (1)°
V = 2004.7 (3) Å^3
Z = 4
F(000) = 832
D_x = 1.274 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1052 reflections
θ = 2.8–22.8°

μ = 0.10 mm^{-1}
T = 298 K

Block, colourless
0.40 × 0.32 × 0.29 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.961, T_{max} = 0.971
4837 measured reflections

1749 independent reflections
947 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 25.1°, θ_{min} = 2.8°
h = −16→15
k = −12→11
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.083
$wR(F^2)$ = 0.280
S = 1.02
1749 reflections
123 parameters
6 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1395P)^2 + 3.7847P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
N1	0.9937 (3)	0.6120 (4)	0.3964 (3)	0.0764 (14)
H1A	1.0180	0.6664	0.3574	0.092*
H1B	1.0312	0.5752	0.4377	0.092*
N2	0.8445 (3)	0.6436 (4)	0.3289 (3)	0.0651 (12)
H2A	0.8709	0.6975	0.2908	0.078*
H2B	0.7824	0.6279	0.3250	0.078*
N3	0.8641 (3)	0.5040 (4)	0.4562 (3)	0.0753 (14)
N4	0.7163 (3)	0.4414 (5)	0.5183 (3)	0.0787 (14)
N5	0.7482 (3)	0.3984 (4)	0.3619 (3)	0.0663 (12)
H5A	0.6934	0.3578	0.3579	0.080*
H5B	0.7857	0.4044	0.3128	0.080*
O1	0.43093 (19)	0.6744 (3)	0.7084 (2)	0.0513 (9)
O2	0.5000	0.4941 (4)	0.7500	0.0802 (17)
O3	0.3680 (3)	0.3385 (6)	0.6850 (5)	0.143 (2)
H3	0.4110	0.3854	0.7063	0.214*
C1	0.8990 (3)	0.5850 (5)	0.3931 (3)	0.0584 (12)
C2	0.7748 (3)	0.4516 (5)	0.4435 (3)	0.0627 (14)
C3	0.6269 (4)	0.3681 (7)	0.5153 (4)	0.095 (2)
H3A	0.5800	0.4085	0.4737	0.143*

H3B	0.6001	0.3621	0.5785	0.143*
H3C	0.6410	0.2847	0.4917	0.143*
C4	0.7393 (6)	0.5018 (9)	0.6077 (5)	0.127 (3)
H4A	0.8000	0.5476	0.6020	0.191*
H4B	0.7458	0.4389	0.6568	0.191*
H4C	0.6873	0.5594	0.6240	0.191*
C5	0.3996 (9)	0.2845 (15)	0.6049 (14)	0.279 (10)
H5D	0.3442	0.2644	0.5646	0.419*
H5E	0.4349	0.2084	0.6203	0.419*
H5F	0.4424	0.3419	0.5719	0.419*
C6	0.5000	0.6130 (5)	0.7500	0.0422 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.055 (2)	0.092 (3)	0.082 (3)	−0.035 (2)	−0.022 (2)	0.034 (2)
N2	0.050 (2)	0.079 (3)	0.067 (3)	−0.0205 (19)	−0.0089 (19)	0.017 (2)
N3	0.065 (3)	0.104 (3)	0.056 (2)	−0.049 (2)	−0.0220 (19)	0.023 (2)
N4	0.076 (3)	0.108 (4)	0.051 (3)	−0.041 (3)	0.000 (2)	−0.003 (2)
N5	0.058 (2)	0.093 (3)	0.047 (2)	−0.034 (2)	−0.0063 (17)	0.000 (2)
O1	0.0389 (15)	0.0469 (17)	0.068 (2)	−0.0007 (12)	−0.0176 (13)	−0.0020 (14)
O2	0.060 (3)	0.037 (3)	0.144 (5)	0.000	−0.032 (3)	0.000
O3	0.063 (3)	0.135 (4)	0.230 (7)	−0.016 (3)	0.011 (3)	−0.097 (4)
C1	0.051 (3)	0.076 (3)	0.048 (2)	−0.024 (2)	−0.009 (2)	0.006 (2)
C2	0.059 (3)	0.079 (3)	0.050 (3)	−0.032 (2)	−0.012 (2)	0.015 (2)
C3	0.076 (4)	0.133 (5)	0.077 (4)	−0.048 (4)	0.007 (3)	0.010 (4)
C4	0.140 (6)	0.180 (8)	0.062 (4)	−0.046 (6)	0.006 (4)	−0.028 (5)
C5	0.153 (9)	0.254 (15)	0.43 (2)	−0.090 (10)	0.122 (12)	−0.223 (16)
C6	0.029 (3)	0.039 (3)	0.059 (4)	0.000	−0.007 (2)	0.000

Geometric parameters (Å, º)

N1—C1	1.317 (6)	C6—O1	1.276 (4)
N1—H1A	0.8600	C6—O2	1.257 (7)
N1—H1B	0.8600	O3—C5	1.330 (13)
N2—C1	1.314 (6)	O3—H3	0.8200
N2—H2A	0.8600	C3—H3A	0.9600
N2—H2B	0.8600	C3—H3B	0.9600
N3—C1	1.319 (6)	C3—H3C	0.9600
N3—C2	1.344 (5)	C4—H4A	0.9600
N4—C2	1.321 (6)	C4—H4B	0.9600
N4—C4	1.436 (8)	C4—H4C	0.9600
N4—C3	1.440 (6)	C5—H5D	0.9600
N5—C2	1.320 (6)	C5—H5E	0.9600
N5—H5A	0.8600	C5—H5F	0.9600
N5—H5B	0.8600	C6—O1^{i}	1.276 (4)
C1—N1—H1A	120.0	N4—C3—H3B	109.5

C1—N1—H1B	120.0	H3A—C3—H3B	109.5
H1A—N1—H1B	120.0	N4—C3—H3C	109.5
C1—N2—H2A	120.0	H3A—C3—H3C	109.5
C1—N2—H2B	120.0	H3B—C3—H3C	109.5
H2A—N2—H2B	120.0	N4—C4—H4A	109.5
C1—N3—C2	120.4 (4)	N4—C4—H4B	109.5
C2—N4—C4	121.7 (5)	H4A—C4—H4B	109.5
C2—N4—C3	122.1 (4)	N4—C4—H4C	109.5
C4—N4—C3	116.2 (5)	H4A—C4—H4C	109.5
C2—N5—H5A	120.0	H4B—C4—H4C	109.5
C2—N5—H5B	120.0	O3—C5—H5D	109.5
H5A—N5—H5B	120.0	O3—C5—H5E	109.5
C5—O3—H3	109.5	H5D—C5—H5E	109.5
N2—C1—N1	117.9 (4)	O3—C5—H5F	109.5
N2—C1—N3	124.0 (4)	H5D—C5—H5F	109.5
N1—C1—N3	118.1 (4)	H5E—C5—H5F	109.5
N5—C2—N4	119.2 (4)	O2—C6—O1^{i}	120.5 (2)
N5—C2—N3	122.0 (4)	O2—C6—O1	120.5 (2)
N4—C2—N3	118.4 (4)	O1^{i}—C6—O1	119.0 (5)
N4—C3—H3A	109.5		

C2—N3—C1—N2	17.2 (8)	C4—N4—C2—N3	9.8 (9)
C2—N3—C1—N1	−165.0 (5)	C3—N4—C2—N3	−169.3 (6)
C4—N4—C2—N5	−177.3 (7)	C1—N3—C2—N5	49.6 (8)
C3—N4—C2—N5	3.6 (9)	C1—N3—C2—N4	−137.7 (6)

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{ii}	0.86	2.04	2.883 (5)	166
N1—H1*B*···N3^{iii}	0.86	2.21	3.069 (6)	175
N2—H2*A*···O1^{iv}	0.86	1.96	2.818 (5)	178
N2—H2*B*···O3^{v}	0.86	2.08	2.896 (6)	159
N5—H5*A*···O1^{v}	0.86	1.95	2.728 (4)	150
O3—H3···O2	0.82	1.77	2.591 (5)	177

Symmetry codes: (ii) −*x*+3/2, −*y*+3/2, −*z*+1; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) *x*+1/2, −*y*+3/2, *z*−1/2; (v) −*x*+1, −*y*+1, −*z*+1.