Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The energetic double salt nitroguanidinium nitrate–guanidinium nitrate (1/1)

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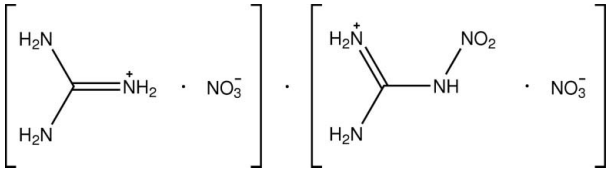
Received 9 May 2007; accepted 30 May 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(N–C) = 0.003 Å; R factor = 0.028; wR factor = 0.054; data-to-parameter ratio = 7.7.

The title compound, $CH_5N_4O_2^+\cdot CH_6N_3^+\cdot 2NO_3^-$, consists of alternating layers of guanidinium and nitroguanidinium cations, these cations being parallel to each other within the layers and perpendicular in adjacent layers. The layers are connected by N—H···O hydrogen bonds to nitrate anions, forming an infinite three-dimensional framework. These hydrogen-bond patterns are closely related to those of guanidinium nitrate.

Related literature

For related literature and structures, see: Bernstein *et al.* (1995); Bryden *et al.* (1956); Haas *et al.* (1965); Hiskey *et al.* (2005); Jeffrey (1997); Katrusiak & Szafrański (1994, 1996); Pace & Flippen-Anderson (1984).



Experimental

Crystal data

$CH_5N_4O_2^+\cdot CH_6N_3^+\cdot 2NO_3^-$
M_r = 289.17
Monoclinic, *Cc*
a = 12.7337 (11) Å
b = 6.9096 (6) Å
c = 13.7852 (13) Å
β = 115.623 (11)°
V = 1093.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 100 (2) K
0.29 × 0.2 × 0.17 mm

Data collection

Oxford Diffraction Xcalibur3 CCD area-detector diffractometer
Absorption correction: multi-scan (*ABSPACK*; Oxford Diffraction, 2006)
T_{min} = 0.894, T_{max} = 0.970
4546 measured reflections
1586 independent reflections
1116 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.054
S = 0.88
1586 reflections
205 parameters
2 restraints
Only H-atom coordinates refined
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O4^{i}	0.87 (3)	2.59 (3)	3.287 (3)	138 (2)
N1—H1A···O5^{i}	0.87 (3)	2.23 (3)	3.058 (3)	157 (2)
N1—H1B···O6^{ii}	0.84 (3)	2.14 (3)	2.956 (3)	164 (2)
N2—H2B···O3^{i}	0.88 (3)	2.63 (3)	3.199 (3)	123 (2)
N2—H2B···O4^{i}	0.88 (3)	2.13 (3)	2.952 (2)	155 (2)
N2—H2A···O6^{iii}	0.75 (2)	2.17 (3)	2.910 (2)	169 (3)
N3—H3B···O4^{ii}	0.84 (3)	2.04 (3)	2.880 (3)	175 (3)
N3—H3A···O5^{iii}	0.86 (2)	2.13 (2)	2.988 (2)	179 (2)
N6—H7···O2^{iv}	0.87 (3)	2.07 (3)	2.928 (3)	170 (2)
N6—H8···O3	0.84 (3)	2.09 (3)	2.897 (2)	161 (2)
N7—H11···O1	0.87 (3)	1.92 (3)	2.766 (2)	165 (3)
N8—H9···O1^{iv}	0.87 (3)	2.09 (3)	2.954 (3)	174 (2)
N8—H10···O3^{v}	0.74 (3)	2.39 (3)	3.069 (2)	153 (3)
N8—H10···O7	0.74 (3)	2.19 (3)	2.660 (3)	122 (3)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *ORTEP-3*.

The authors thank Matthias Scherr, Peter Mayer and Jörg Stierstorfer for the data collection and helpful discussion. Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Fonds der Chemischen Industrie (FCI), the European Research Office (ERO) of the US Army Research Laboratory (ARL) under contract Nos. N 62558-05-C-0027 and 9939-AN-01, and the Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants (WIWEB) under contract Nos. E/E210/4D004/X5143 and E/E210/7D002/4 F088, is gratefully acknowledged. Georg Steinhauser thanks the Austrian Science Fund (FWF) for financial support (Erwin Schrödinger Auslandsstipendium, project No. J2645-N17).

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  doi:10.1107/S1600536807026451

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2037).

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supplementary materials

Acta Cryst. (2007). E**63**, o3100-o3101 [**doi:10.1107/S1600536807026451**]

The energetic double salt nitroguanidinium nitrate-guanidinium nitrate (1/1)

G. Steinhauser, M.-J. Crawford, C. Darwich, T. M. Klapötke, C. Miró Sabaté and J. M. Welch

Comment

Guanidinium and nitroguanidinium compounds are objects of investigation for a possible application as energetic materials (*e.g.*, Hiskey *et al.*, 2005; Pace & Flippen-Anderson, 1984). The crystal structures of guanidinium nitrate (GN) (Katrusiak & Szafrański, 1994, 1996) and nitroguanidinium nitrate (NGN) (Pace & Flippen-Anderson, 1984) have been determined previously. Here, we report the structure of a new nitroguanidinium nitrate-guanidinium nitrate (NGN-GN) double salt.

As for every potential energetic material, a high density is desired. The density of NGN-GN – 1.757 g.cm^{-3} (100 K) – is comparable to that of NGN (1.80 g.cm^{-3}; Pace & Flippen-Anderson, 1984), and significantly higher than that of the three phases of GN (GN1, GN2 and GN3). The respective densities are for GN1: 1.458 g.cm^{-3} (153 K), 1.443 g.cm^{-3} (185 K), 1.421 g.cm^{-3} (257 K), 1.410 g.cm^{-3} (291 K), for GN2: 1.444 g.cm^{-3} (292 K), and for GN3: 1.400 (391 K) (Katrusiak & Szafrański, 1996).

NGN-GN contains one guanidinium and one nitroguanidinium ion and two nitrate counter-ions. The compound consists of alternating, perpendicular layers of guanidinium and nitroguanidinium cations.

The bond lengths in the guanidinium ion are similar to those found in guanidinium chloride (Haas *et al.*, 1965). The geometry of the nitroguanidinium ion is similar to that in Bryden *et al.* (1956) and Pace & Flippen-Anderson (1984).

H-bonds in NGN-GN are medium to weak according to Jeffrey (1997). The only ring pattern observed is R2,2(8), and a variety of chain patterns are also observed: C2,2(6), C2,2(8) and C1,2(6) (Bernstein *et al.*, 1995). An intramolecular H-bond is also present (N8–H10···O7).

Experimental

NGN-GN formed in a side reaction using 4.00 g (17 mmol) copper(II) nitrate pentahemihydrate, 6.30 g GN (52 mmol) and 4.5 ml of concentrated HNO_3 at 373 K. Single crystals of the compound were obtained upon evaporation of HNO_3.

Refinement

Because no strong anomalously scattering atoms are present the absolute structure cannot be determined and therefore, Friedel opposites were merged in the refinement.

H atoms were located in Fourier difference maps and their coordinates were refined with U_{iso} fixed at 0.03 Å.

Figures

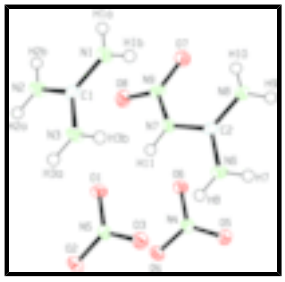

Fig. 1. Molecular structure of NGN-GN with labelling and displacement ellipsoids drawn at the 50% probability level.

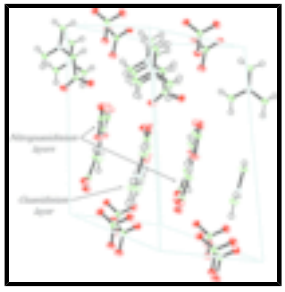

Fig. 2. Crystal structure of NGN-GN showing the layers of guanidinium alternating with layers of nitroguanidinium (the nitroguanidinium cations are eclipsed by the guanidinum ions on the subsequent layer).

nitroguanidinium nitrate–guanidinium nitrate (1/1)

Crystal data

$CH_5N_4O_2^+ \cdot CH_6N_3^+ \cdot 2NO_3^-$	$Z = 4$
$M_r = 289.17$	$F_{000} = 600$
Monoclinic, *Cc*	$D_x = 1.756$ Mg m^{-3}
Hall symbol: C -2yc	Mo *K*α radiation λ = 0.71073 Å
a = 12.7337 (11) Å	θ = 4.1–30.0º
b = 6.9096 (6) Å	μ = 0.17 mm^{-1}
c = 13.7852 (13) Å	*T* = 100 (2) K
β = 115.623 (11)º	Block, colorless
V = 1093.6 (2) Å^3	0.29 × 0.2 × 0.17 mm

Data collection

Oxford Diffraction Xcalibur3 CCD area-detector diffractometer	1586 independent reflections
Radiation source: fine-focus sealed tube	1116 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.029$
T = 100(2) K	$\theta_{max} = 30.0$º
ω scan	$\theta_{min} = 4.1$º
Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2006 or???2005)	*h* = −17→16
$T_{min} = 0.894$, $T_{max} = 0.970$	*k* = −9→9
4546 measured reflections	*l* = −19→16

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
$wR(F^2) = 0.054$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$S = 0.88$	Extinction correction: none
1586 reflections	
205 parameters	
2 restraints	
Only H-atom coordinates refined	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.08343 (17)	0.1042 (3)	0.20399 (16)	0.0172 (4)
C2	0.34933 (15)	0.2984 (3)	0.14373 (16)	0.0161 (4)
N1	0.18538 (15)	0.0198 (3)	0.26283 (17)	0.0221 (4)
N2	0.03241 (17)	0.2099 (3)	0.25130 (16)	0.0214 (4)
N3	0.03384 (16)	0.0827 (3)	0.09806 (15)	0.0188 (4)
N4	0.24964 (13)	0.8432 (3)	0.03346 (13)	0.0179 (4)
N5	0.01983 (14)	0.5459 (3)	−0.02710 (14)	0.0172 (4)
N6	0.30525 (15)	0.2977 (3)	0.03790 (14)	0.0185 (4)
N7	0.28239 (16)	0.3904 (3)	0.18546 (14)	0.0192 (4)
N8	0.44917 (14)	0.2152 (3)	0.20268 (15)	0.0186 (4)
N9	0.31847 (14)	0.4428 (3)	0.29147 (14)	0.0196 (4)
O1	0.06327 (12)	0.5503 (2)	0.07493 (11)	0.0218 (4)
O2	−0.07552 (12)	0.6259 (2)	−0.08132 (11)	0.0232 (4)
O3	0.07414 (12)	0.4623 (2)	−0.07189 (11)	0.0228 (4)
O4	0.14695 (12)	0.9014 (2)	−0.01956 (12)	0.0224 (4)
O5	0.30983 (12)	0.7982 (2)	−0.01384 (12)	0.0272 (4)
O6	0.29080 (12)	0.8303 (2)	0.13394 (12)	0.0250 (4)
O7	0.41354 (12)	0.3896 (2)	0.35785 (12)	0.0240 (4)
O8	0.24830 (12)	0.5406 (2)	0.30883 (12)	0.0249 (4)
H1A	0.217 (2)	0.040 (4)	0.332 (2)	0.030*
H1B	0.221 (2)	−0.049 (4)	0.237 (2)	0.030*
H2A	−0.026 (2)	0.251 (4)	0.217 (2)	0.030*
H2B	0.064 (2)	0.216 (4)	0.322 (2)	0.030*
H3A	−0.031 (2)	0.144 (3)	0.065 (2)	0.030*

H3B	0.071 (2)	0.029 (4)	0.067 (2)	0.030*
H7	0.347 (2)	0.241 (4)	0.010 (2)	0.030*
H8	0.247 (2)	0.366 (4)	0.002 (2)	0.030*
H9	0.486 (2)	0.162 (4)	0.170 (2)	0.030*
H10	0.472 (2)	0.206 (4)	0.262 (2)	0.030*
H11	0.219 (2)	0.450 (4)	0.143 (2)	0.030*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0179 (9)	0.0184 (11)	0.0169 (11)	−0.0031 (9)	0.0092 (9)	0.0016 (9)
C2	0.0173 (10)	0.0144 (10)	0.0167 (11)	−0.0025 (8)	0.0075 (9)	0.0022 (9)
N1	0.0169 (8)	0.0331 (12)	0.0146 (9)	0.0037 (8)	0.0053 (7)	0.0008 (9)
N2	0.0197 (9)	0.0282 (11)	0.0141 (9)	0.0051 (8)	0.0052 (8)	−0.0002 (9)
N3	0.0182 (9)	0.0231 (10)	0.0126 (9)	0.0049 (8)	0.0043 (7)	−0.0006 (8)
N4	0.0167 (9)	0.0192 (9)	0.0166 (10)	−0.0025 (7)	0.0061 (8)	−0.0009 (8)
N5	0.0130 (8)	0.0206 (10)	0.0163 (10)	−0.0022 (7)	0.0048 (7)	−0.0008 (8)
N6	0.0187 (9)	0.0233 (10)	0.0114 (9)	0.0021 (7)	0.0047 (7)	0.0005 (8)
N7	0.0143 (8)	0.0281 (10)	0.0128 (10)	0.0023 (7)	0.0036 (7)	−0.0008 (8)
N8	0.0170 (8)	0.0262 (10)	0.0131 (8)	0.0024 (8)	0.0070 (7)	0.0017 (9)
N9	0.0213 (10)	0.0238 (10)	0.0124 (9)	−0.0043 (7)	0.0060 (8)	−0.0013 (8)
O1	0.0197 (7)	0.0304 (9)	0.0130 (8)	0.0030 (7)	0.0050 (6)	0.0013 (7)
O2	0.0151 (7)	0.0295 (8)	0.0205 (8)	0.0026 (7)	0.0033 (6)	0.0028 (7)
O3	0.0194 (7)	0.0291 (8)	0.0192 (8)	0.0030 (7)	0.0078 (7)	−0.0025 (7)
O4	0.0156 (7)	0.0307 (9)	0.0175 (8)	0.0042 (6)	0.0041 (6)	−0.0010 (7)
O5	0.0219 (8)	0.0424 (10)	0.0206 (9)	0.0074 (7)	0.0123 (7)	0.0028 (8)
O6	0.0189 (7)	0.0390 (10)	0.0160 (8)	0.0042 (7)	0.0066 (6)	0.0005 (7)
O7	0.0167 (7)	0.0375 (9)	0.0156 (8)	−0.0007 (7)	0.0049 (6)	0.0002 (7)
O8	0.0249 (7)	0.0314 (8)	0.0218 (8)	0.0031 (7)	0.0134 (6)	−0.0031 (8)

Geometric parameters (Å, °)

C1—N2	1.322 (3)	N4—O6	1.254 (2)
C1—N3	1.325 (3)	N4—O4	1.257 (2)
C1—N1	1.332 (3)	N5—O2	1.246 (2)
C2—N8	1.309 (3)	N5—O3	1.250 (2)
C2—N6	1.317 (3)	N5—O1	1.270 (2)
C2—N7	1.373 (3)	N6—H7	0.87 (3)
N1—H1A	0.87 (3)	N6—H8	0.84 (3)
N1—H1B	0.84 (3)	N7—N9	1.377 (2)
N2—H2A	0.75 (2)	N7—H11	0.87 (3)
N2—H2B	0.88 (3)	N8—H9	0.87 (3)
N3—H3A	0.86 (2)	N8—H10	0.74 (3)
N3—H3B	0.84 (3)	N9—O7	1.216 (2)
N4—O5	1.241 (2)	N9—O8	1.224 (2)
N2—C1—N3	120.3 (2)	O6—N4—O4	119.86 (18)
N2—C1—N1	120.0 (2)	O2—N5—O3	120.81 (18)
N3—C1—N1	119.8 (2)	O2—N5—O1	119.89 (19)

N8—C2—N6	121.4 (2)	O3—N5—O1	119.30 (17)
N8—C2—N7	123.7 (2)	C2—N6—H7	116.1 (16)
N6—C2—N7	114.90 (18)	C2—N6—H8	119.8 (19)
C1—N1—H1A	117.5 (17)	H7—N6—H8	123 (3)
C1—N1—H1B	123.9 (17)	C2—N7—N9	125.70 (17)
H1A—N1—H1B	119 (2)	C2—N7—H11	120.4 (18)
C1—N2—H2A	118 (2)	N9—N7—H11	111.8 (18)
C1—N2—H2B	119.0 (17)	C2—N8—H9	117.6 (16)
H2A—N2—H2B	122 (3)	C2—N8—H10	123 (2)
C1—N3—H3A	114.5 (17)	H9—N8—H10	119 (3)
C1—N3—H3B	120.1 (18)	O7—N9—O8	126.37 (18)
H3A—N3—H3B	125 (3)	O7—N9—N7	119.05 (18)
O5—N4—O6	120.27 (16)	O8—N9—N7	114.58 (16)
O5—N4—O4	119.87 (17)		
N8—C2—N7—N9	13.7 (3)	C2—N7—N9—O7	−7.4 (3)
N6—C2—N7—N9	−166.8 (2)	C2—N7—N9—O8	172.97 (18)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O4^{i}	0.87 (3)	2.59 (3)	3.287 (3)	138 (2)
N1—H1A···O5^{i}	0.87 (3)	2.23 (3)	3.058 (3)	157 (2)
N1—H1B···O6^{ii}	0.84 (3)	2.14 (3)	2.956 (3)	164 (2)
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N2—H2B···O4^{i}	0.88 (3)	2.13 (3)	2.952 (2)	155 (2)
N2—H2A···O6^{iii}	0.75 (2)	2.17 (3)	2.910 (2)	169 (3)
N3—H3B···O4^{ii}	0.84 (3)	2.04 (3)	2.880 (3)	175 (3)
N3—H3A···O5^{iii}	0.86 (2)	2.13 (2)	2.988 (2)	179 (2)
N6—H7···O2^{iv}	0.87 (3)	2.07 (3)	2.928 (3)	170 (2)
N6—H8···O3	0.84 (3)	2.09 (3)	2.897 (2)	161 (2)
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N8—H9···O1^{iv}	0.87 (3)	2.09 (3)	2.954 (3)	174 (2)
N8—H10···O3^{v}	0.74 (3)	2.39 (3)	3.069 (2)	153 (3)
N8—H10···O7	0.74 (3)	2.19 (3)	2.660 (3)	122 (3)

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

Fig. 1

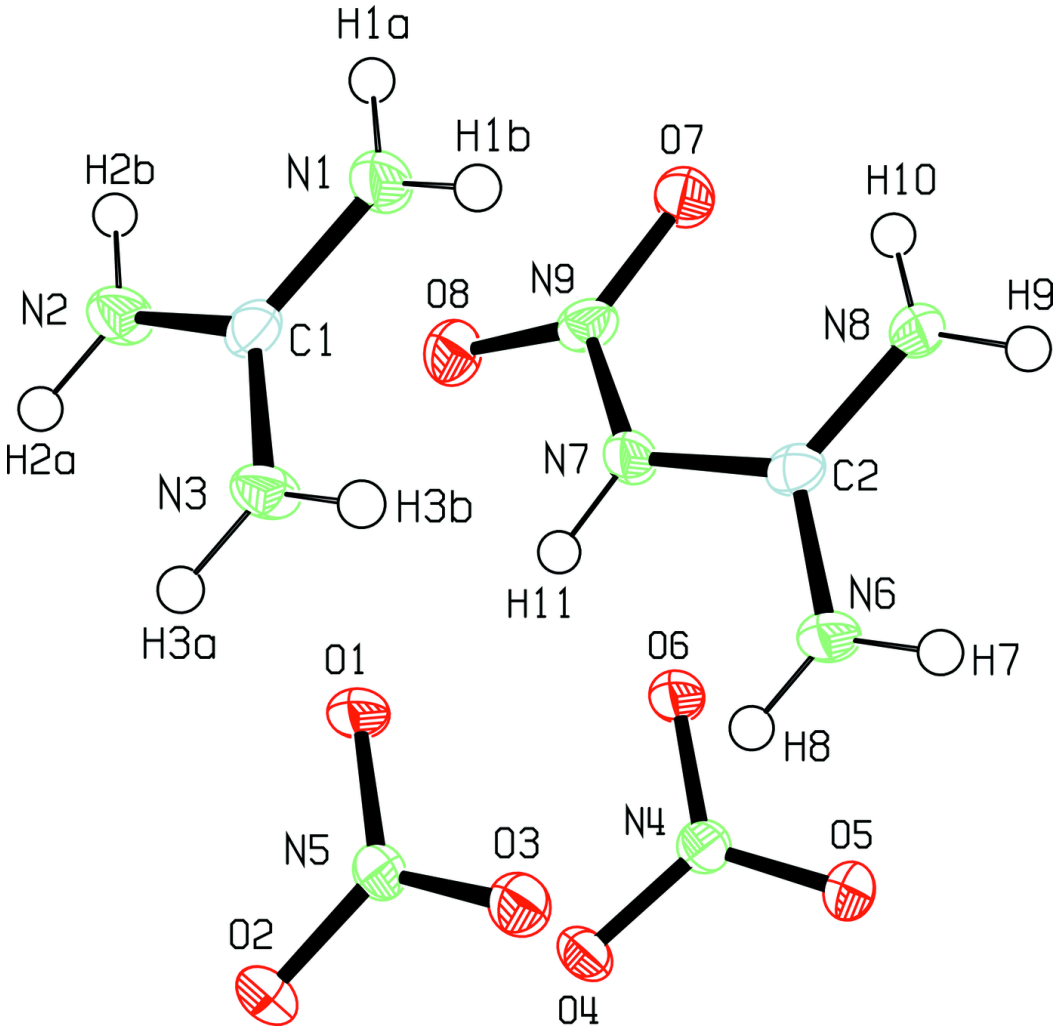
H1a
H1b
N1
H2b
N2
C1
H2a
N3
H3b
H3a
O7
H10
O8
N9
N8
H9
N7
C2
H11
N6
H7
H8
O1
O6
N5
O3
N4
O5
O2
O4

Fig. 2