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Urea–*N*,*N*-dimethylformamide (3/1)

Philippe Fernandes,[a] Alastair J. Florence,[a]* Francesca Fabbiani,[b] William I. F. David[b] and Kenneth Shankland[b]

[a]Solid-State Research Group, Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, and [b]ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England
Correspondence e-mail: alastair.florence@strath.ac.uk

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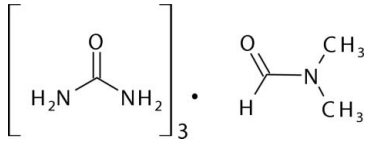
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(N–C) = 0.002 Å; R factor = 0.039; wR factor = 0.105; data-to-parameter ratio = 16.7.

Urea forms a 3:1 solvate with *N*,*N*-dimethylformamide to give the title compound, $3CH_4N_2O{\cdot}C_3H_7NO$. The structure displays an extensive network of intermolecular hydrogen bonding.

Related literature

For details on the experimental methods used to obtain this form, see: Florence *et al.* (2003). For crystal structures of urea see: Vaughan & Donohue (1952) and references therein; Swaminathan *et al.* (1984); Pryor & Sanger (1970); Guth *et al.* (1980); Weber *et al.* (2002).



Experimental

Crystal data

$3CH_4N_2O{\cdot}C_3H_7NO$
M_r = 253.26
Triclinic, $P\overline{1}$
a = 7.5246 (13) Å
b = 9.866 (4) Å
c = 10.821 (4) Å
α = 65.61 (4)°
β = 79.43 (2)°
γ = 70.76 (2)°
V = 689.7 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 150 K
0.36 × 0.26 × 0.18 mm

Data collection

Oxford Diffraction Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.92, T_{max} = 0.98
14479 measured reflections
3177 independent reflections
2407 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.105
S = 0.98
3177 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 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
N3—H31···O6^{i}	0.903 (17)	2.052 (17)	2.9462 (19)	170.8 (16)
N3—H32···O10^{ii}	0.866 (17)	2.475 (16)	3.195 (2)	141.1 (15)
N4—H41···O17^{iii}	0.872 (19)	2.054 (19)	2.924 (2)	177.0 (14)
N4—H42···O10^{ii}	0.818 (18)	2.131 (18)	2.920 (2)	162.1 (16)
N7—H71···O10	0.853 (19)	2.05 (2)	2.894 (2)	170.4 (16)
N7—H72···O17^{iv}	0.838 (18)	2.136 (18)	2.969 (2)	172.8 (17)
N8—H81···O2^{v}	0.887 (17)	2.014 (17)	2.8935 (18)	171.4 (16)
N8—H82···O2^{vi}	0.851 (18)	2.13 (2)	2.903 (2)	150.5 (15)
N11—H111···O2^{vii}	0.839 (17)	2.028 (16)	2.8435 (19)	163.8 (17)
N11—H112···O10^{viii}	0.894 (16)	2.018 (16)	2.9103 (19)	175.6 (17)
N12—H121···O2^{vii}	0.842 (17)	2.568 (18)	3.247 (2)	138.6 (14)
N12—H122···O6	0.863 (17)	2.074 (17)	2.926 (2)	169.7 (14)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z$; (iv) $x, y-1, z+1$; (v) $x+1, y, z$; (vi) $-x+1, -y, -z+1$; (vii) $-x, -y+1, -z+1$; (viii) $-x+1, -y+1, -z+2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED*; data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2065).

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supplementary materials

Acta Cryst. (2007). E**63**, o4861 [**doi:10.1107/S1600536807059934**]

Urea-*N,N*-dimethylformamide (3/1)

P. Fernandes, A. J. Florence, F. Fabbiani, W. I. F. David and K. Shankland

Comment

The crystal structure of urea has been widely studied (see for example, Vaughan and Donohue (1952) and references therein; Swaminathan *et al.* (1984), Pryor and Sanger (1970), Guth *et al.* (1980) and Weber *et al.* (2002)). This novel crystalline solvate of urea was discovered during an investigation into the influence of different crystallization solvents on urea crystal morphology. A sample was obtained by slow evaporation of a saturated *N,N*-dimethyl formamide (DMF) solution at 298 K and identified as a novel form using multi-sample foil transmission X-ray powder diffraction analysis (Florence *et al.*, 2003). Subsequent recrystallization produced a single-crystal suitable for X-ray diffraction at 150 K (Fig. 1). The compound crystallizes in space group $P\bar{1}$ with three molecules of urea and one molecule of DMF in the asymmetric unit. The molecules comprising this structure offer a relatively large number of potential hydrogen bond donors (4 N—H groups in urea) and acceptors (1 carbonyl O-atom in urea and in DMF), hence it is not surprising to observe that molecular packing results in an extensive three dimensional hydrogen bonded network (Fig. 2) comprising 12 unique N—H···O hydrogen bonds (Table 1).

Experimental

The compound was sourced from Sigma-Aldrich and used as supplied. A single-crystal sample of the 3/1 solvate was recrystallized from a saturated *N,N*-dimethyl formamide solution by isothermal solvent evaporation at room temperature.

Refinement

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 N—H to 0.86 O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The positions of H atoms attached to nitrogen were refined freely.

Figures

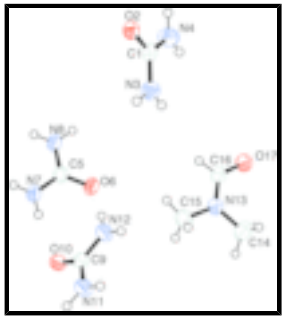

Fig. 1. The asymmetric unit of the title compound showing 50% probablility displacement ellipsoids.

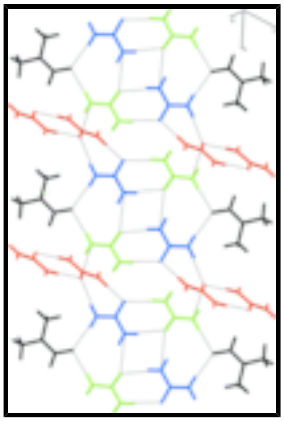

Fig. 2. Molecular packing in the structure of the urea DMF (3/1) solvate illustrating the extended hydrogen bonded network. Molecules colour coded according to symmetry equivalence (DMF = black) and hydrogen bonds are shown as dashed lines.

#Diaminomethanal *N*,*N*-dimethylformamide (3/1) Urea *N*,*N*-dimethylformamide (3/1)

Crystal data

$3CH_4N_2O{\cdot}C_3H_7NO$	$Z = 2$
$M_r = 253.26$	$F_{000} = 272$
Triclinic, $P\overline{1}$	$D_x = 1.219$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.5246$ (13) Å	Cell parameters from 6184 reflections
$b = 9.866$ (4) Å	$\theta = 3$–29º
$c = 10.821$ (4) Å	$\mu = 0.10$ mm^{-1}
$\alpha = 65.61$ (4)º	$T = 150$ K
$\beta = 79.43$ (2)º	Block, colourless
$\gamma = 70.76$ (2)º	0.36 × 0.26 × 0.18 mm
$V = 689.7$ (5) Å^3	

Data collection

Oxford Diffraction Gemini diffractometer	2407 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.022$
$T = 150$ K	$\theta_{max} = 28.6$º
φ & ω scans	$\theta_{min} = 2.9$º
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (Oxford Diffraction, 2006).	$h = -9\rightarrow10$
$T_{min} = 0.92$, $T_{max} = 0.98$	$k = -11\rightarrow13$
14479 measured reflections	$l = 0\rightarrow14$
3177 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.039$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.06P)^2 + 0.11P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{max} = 0.0002$
$S = 0.98$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
3177 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
190 parameters	Extinction correction: None
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.06958 (17)	0.32108 (13)	0.27505 (12)	0.0356
O2	−0.02843 (12)	0.22791 (9)	0.31656 (8)	0.0371
N3	0.06236 (17)	0.41092 (13)	0.34153 (12)	0.0435
N4	0.18100 (18)	0.33455 (16)	0.16228 (12)	0.0504
C5	0.82167 (18)	0.21738 (14)	0.65710 (12)	0.0388
O6	0.79384 (13)	0.35798 (9)	0.57991 (8)	0.0446
N7	0.78236 (18)	0.17494 (14)	0.79088 (11)	0.0466
N8	0.89032 (19)	0.10598 (13)	0.60730 (12)	0.0507
C9	0.47338 (17)	0.53430 (13)	0.79962 (12)	0.0348
O10	0.62105 (12)	0.44582 (10)	0.86052 (8)	0.0396
N11	0.33423 (16)	0.61656 (14)	0.85785 (12)	0.0417
N12	0.45371 (18)	0.54772 (14)	0.67442 (11)	0.0434
N13	0.71303 (17)	0.86268 (13)	0.19938 (11)	0.0456
C14	0.6913 (3)	1.02738 (19)	0.15339 (18)	0.0769
C15	0.6756 (2)	0.78009 (19)	0.34263 (14)	0.0542
C16	0.7682 (2)	0.79285 (16)	0.11316 (13)	0.0511
O17	0.80099 (19)	0.85536 (12)	−0.00986 (10)	0.0654
H31	−0.013 (2)	0.3994 (18)	0.4182 (17)	0.0537*
H32	0.134 (2)	0.4718 (19)	0.3162 (16)	0.0533*
H41	0.184 (2)	0.276 (2)	0.1193 (17)	0.0631*
H42	0.242 (2)	0.397 (2)	0.1383 (17)	0.0639*
H71	0.740 (2)	0.248 (2)	0.8206 (16)	0.0528*
H72	0.792 (2)	0.082 (2)	0.8414 (16)	0.0532*
H81	0.911 (2)	0.1357 (19)	0.5179 (17)	0.0558*
H82	0.914 (2)	0.010 (2)	0.6577 (16)	0.0550*
H111	0.237 (2)	0.6740 (18)	0.8152 (16)	0.0488*
H112	0.349 (2)	0.6023 (18)	0.9429 (16)	0.0490*
H121	0.356 (2)	0.6083 (19)	0.6330 (16)	0.0504*
H122	0.545 (2)	0.4918 (18)	0.6397 (15)	0.0503*

H141	0.7800	1.0627	0.0811	0.1148*
H142	0.7014	1.0559	0.2241	0.1142*
H143	0.5751	1.0767	0.1163	0.1149*
H151	0.6989	0.6705	0.3617	0.0800*
H152	0.7550	0.7932	0.3944	0.0794*
H153	0.5484	0.8217	0.3689	0.0802*
H161	0.7785	0.6845	0.1534	0.0614*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0382 (6)	0.0325 (6)	0.0306 (6)	−0.0081 (5)	−0.0049 (5)	−0.0068 (5)
O2	0.0434 (5)	0.0330 (4)	0.0319 (4)	−0.0130 (4)	−0.0007 (3)	−0.0083 (3)
N3	0.0505 (7)	0.0423 (6)	0.0421 (6)	−0.0206 (5)	0.0041 (5)	−0.0172 (5)
N4	0.0605 (8)	0.0594 (7)	0.0427 (6)	−0.0342 (6)	0.0134 (5)	−0.0237 (6)
C5	0.0441 (7)	0.0340 (6)	0.0336 (6)	−0.0109 (5)	0.0026 (5)	−0.0102 (5)
O6	0.0583 (6)	0.0297 (4)	0.0351 (5)	−0.0093 (4)	0.0077 (4)	−0.0086 (4)
N7	0.0675 (8)	0.0322 (6)	0.0321 (6)	−0.0123 (5)	0.0043 (5)	−0.0089 (5)
N8	0.0777 (9)	0.0296 (5)	0.0339 (6)	−0.0106 (5)	0.0065 (5)	−0.0091 (5)
C9	0.0399 (6)	0.0323 (6)	0.0339 (6)	−0.0147 (5)	−0.0013 (5)	−0.0111 (5)
O10	0.0418 (5)	0.0411 (5)	0.0370 (4)	−0.0074 (4)	−0.0046 (4)	−0.0180 (4)
N11	0.0391 (6)	0.0469 (6)	0.0368 (6)	−0.0050 (5)	−0.0050 (5)	−0.0181 (5)
N12	0.0454 (6)	0.0468 (6)	0.0346 (6)	−0.0058 (5)	−0.0064 (5)	−0.0159 (5)
N13	0.0590 (7)	0.0390 (6)	0.0354 (5)	−0.0152 (5)	−0.0027 (5)	−0.0100 (5)
C14	0.1287 (17)	0.0406 (8)	0.0538 (9)	−0.0175 (10)	−0.0026 (10)	−0.0168 (7)
C15	0.0661 (9)	0.0586 (9)	0.0366 (7)	−0.0247 (7)	0.0026 (6)	−0.0136 (6)
C16	0.0771 (10)	0.0361 (7)	0.0378 (7)	−0.0204 (7)	−0.0024 (7)	−0.0088 (6)
O17	0.1138 (10)	0.0459 (6)	0.0351 (5)	−0.0294 (6)	0.0023 (5)	−0.0116 (4)

Geometric parameters (Å, °)

C1—O2	1.2550 (15)	C9—N12	1.3369 (17)
C1—N3	1.3367 (17)	N11—H111	0.841 (16)
C1—N4	1.3317 (17)	N11—H112	0.895 (16)
N3—H31	0.903 (17)	N12—H121	0.844 (17)
N3—H32	0.868 (16)	N12—H122	0.863 (16)
N4—H41	0.877 (18)	N13—C14	1.450 (2)
N4—H42	0.817 (18)	N13—C15	1.4471 (18)
C5—O6	1.2577 (16)	N13—C16	1.3106 (18)
C5—N7	1.3350 (17)	C14—H141	0.957
C5—N8	1.3333 (17)	C14—H142	0.940
N7—H71	0.854 (17)	C14—H143	0.922
N7—H72	0.837 (17)	C15—H151	0.973
N8—H81	0.887 (17)	C15—H152	0.960
N8—H82	0.852 (17)	C15—H153	0.950
C9—O10	1.2592 (15)	C16—O17	1.2309 (17)
C9—N11	1.3312 (17)	C16—H161	0.955
O2—C1—N3	120.88 (11)	H111—N11—H112	124.4 (15)

O2—C1—N4	120.68 (12)	C9—N12—H121	120.4 (11)
N3—C1—N4	118.42 (12)	C9—N12—H122	116.7 (10)
C1—N3—H31	117.1 (10)	H121—N12—H122	122.9 (15)
C1—N3—H32	121.5 (11)	C14—N13—C15	117.53 (13)
H31—N3—H32	121.2 (14)	C14—N13—C16	120.28 (12)
C1—N4—H41	117.5 (11)	C15—N13—C16	122.18 (12)
C1—N4—H42	117.8 (12)	N13—C14—H141	113.4
H41—N4—H42	124.7 (17)	N13—C14—H142	112.2
O6—C5—N7	121.26 (12)	H141—C14—H142	108.0
O6—C5—N8	120.80 (12)	N13—C14—H143	105.7
N7—C5—N8	117.94 (12)	H141—C14—H143	105.2
C5—N7—H71	116.3 (11)	H142—C14—H143	112.2
C5—N7—H72	121.2 (11)	N13—C15—H151	110.0
H71—N7—H72	122.4 (15)	N13—C15—H152	109.2
C5—N8—H81	117.1 (10)	H151—C15—H152	110.2
C5—N8—H82	122.6 (11)	N13—C15—H153	110.2
H81—N8—H82	120.3 (14)	H151—C15—H153	109.4
O10—C9—N11	120.97 (11)	H152—C15—H153	107.6
O10—C9—N12	120.39 (12)	N13—C16—O17	125.87 (13)
N11—C9—N12	118.64 (12)	N13—C16—H161	113.8
C9—N11—H111	119.0 (11)	O17—C16—H161	120.3
C9—N11—H112	116.6 (10)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H31···O6^{i}	0.903 (17)	2.052 (17)	2.9462 (19)	170.8 (16)
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N11—H111···O2^{vii}	0.839 (17)	2.028 (16)	2.8435 (19)	163.8 (17)
N11—H112···O10^{viii}	0.894 (16)	2.018 (16)	2.9103 (19)	175.6 (17)
N12—H121···O2^{vii}	0.842 (17)	2.568 (18)	3.247 (2)	138.6 (14)
N12—H122···O6	0.863 (17)	2.074 (17)	2.926 (2)	169.7 (14)

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

Fig. 1

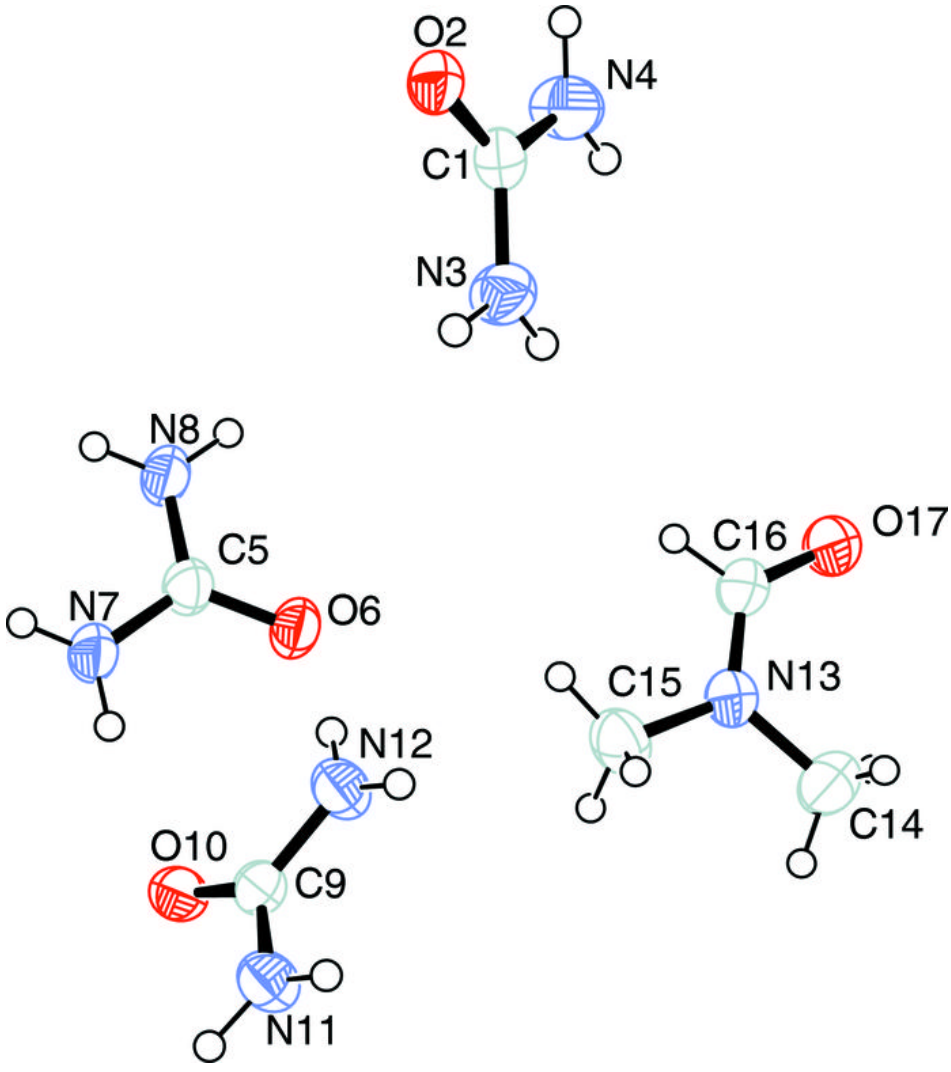

Fig. 2