

cis-Diamminedichloridoplatinum(II) *N,N*-dimethylformamide monosolvate

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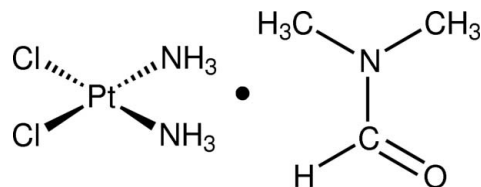
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{O}-\text{C}) = 0.012$ Å; R factor = 0.028; wR factor = 0.072; data-to-parameter ratio = 16.9.

In the title compound, *cis*-[PtCl₂(NH₃)₂] \cdot C₃H₇NO, the metal complex molecules are stacked parallel to the *b* axis, forming close Pt \cdots Pt interactions of 3.4071 (7) and 3.5534 (8) Å and weak N—H \cdots Cl hydrogen bonds between the ammine ligand and the Cl atoms of the neighboring complex. Conventional N—H \cdots O hydrogen bonds are formed between ammine ligands and the O atom of adjacent *N,N*-dimethylformamide molecules. The crystal was found to be a split crystal and was analyzed using two domains related by a rotation of *ca* 4.4° about the reciprocal axis (−0.351 1.000 0.742) and refined to give a minor component fraction of 0.084 (6).

Related literature

For a review of platinum anticancer coordination compounds, see: Reedijk (2009). For the preparation of *cis*-diamminedichloridoplatinum(II), see: Kukushikin *et al.* (1998). For single-crystal X-ray and neutron diffraction studies of *cis*-diamminedichloridoplatinum(II), see: Milburn & Truter (1966); Ting *et al.* (2010). For vibrational studies, see: Nakamoto *et al.* (1965). For crystallographic studies of dimethylformamide solvates and complexes of *cis*-diamminedichloridoplatinum(II) and related compounds, see: Raudaschl *et al.* (1983, 1985); Raudaschl-Sieber *et al.* (1986); Alston *et al.* (1985). For a crystallographic study of palladium analogs, see: Kirik *et al.* (1996). For a detailed analysis of linear chain-structures in platinum(II) complexes, see: Connick *et al.* (1997). For an analysis of hydrogen bonding in platinum–ammine complexes, see: Brammer *et al.* (1987).



Experimental

Crystal data

[PtCl₂(NH₃)₂] \cdot C₃H₇NO
 $M_r = 373.15$
Triclinic, $P\bar{1}$
 $a = 6.2344$ (9) Å
 $b = 6.8196$ (11) Å
 $c = 11.5833$ (18) Å
 $\alpha = 105.285$ (4)°
 $\beta = 96.061$ (4)°

$\gamma = 97.809$ (4)°
 $V = 465.47$ (12) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 15.59$ mm^{−1}
 $T = 200$ K
0.46 × 0.36 × 0.10 mm

Data collection

Bruker SMART X2S benchtop diffractometer
Absorption correction: multi-scan (*TWINABS*; Bruker, 2009)
 $T_{\min} = 0.05$, $T_{\max} = 0.30$

7440 measured reflections
1620 independent reflections
1484 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.072$
 $S = 1.07$
1620 reflections

96 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 1.44$ e Å^{−3}
 $\Delta\rho_{\min} = -2.08$ e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1E \cdots Cl1 ⁱ	0.91	2.51	3.389 (7)	161
N2—H2E \cdots Cl2 ⁱ	0.91	2.53	3.403 (7)	162
N1—H1D \cdots O1 ⁱⁱ	0.91	2.13	3.023 (9)	167
N2—H2F \cdots O1 ⁱⁱⁱ	0.91	2.31	3.198 (9)	165

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

Data collection: *APEX2* and *GIS* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009); molecular graphics: *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *POV-RAY* (Cason, 2004); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2417).

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supplementary materials

Acta Cryst. (2012). E68, m863–m864 [doi:10.1107/S1600536812024014]

***cis*-Diamminedichloridoplatinum(II) *N,N*-dimethylformamide monosolvate**

Dean H. Johnston, Nathanael A. Miller and Cory B. Tackett

Comment

Cis-diamminedichloridoplatinum(II), also known as cisplatin, is a widely used anti-cancer drug that has been extensively studied since its clinical applications were first discovered (Reedijk, 2009). The structure of cisplatin was first determined crystallographically in 1966 (Milburn & Truter, 1966); a recent study has elaborated the structure of the two common polymorphs (Ting *et al.*, 2010). A different DMF-solvate of cisplatin has been described previously (Raudaschl *et al.*, 1983, Raudaschl *et al.* 1985, Raudaschl-Sieber *et al.* 1986). A crown ether complex of cisplatin has also been crystallographically characterized (Alston *et al.*, 1985).

The title compound has a square-planar geometry (Fig. 1) and forms stacked chains along the crystallographic *b* axis with Pt—Pt distances of 3.4071 (7) and 3.5534 (8) Å and Pt—Pt—Pt angle of 156.90 (2) degrees as shown in Figures 2 and 3. Formation of extended platinum chains through stacking is a common motif in square-planar platinum compounds (Connick *et al.*, 1997). Hydrogen bonds are formed between the ammine hydrogen atoms and the chlorine atoms on the closer of the two neighboring complexes. This type of hydrogen bonding has been proposed or observed in previous studies on cisplatin and related complexes (Milburn & Truter, 1966; Brammer *et al.*, 1987; Ting *et al.*, 2010).

Additional hydrogen bonds are formed between the ammine hydrogen atoms and the oxygen atom of the *N,N*-dimethylformamide as illustrated in Figure 4. Similar interactions are seen in the DMF-solvated cisplatin structure previously described (Raudaschl *et al.*, 1983, Raudaschl *et al.*, 1985, Raudaschl-Sieber *et al.*, 1986). Interestingly, the previously described DMF solvate of cisplatin does not display stacking of the metal complexes seen in the title compound.

Experimental

The title complex was prepared by refluxing 2.00 g (4.82 mmol) of K₂[PtCl₄] with 1.60 g (20.8 mmol) of ammonium acetate and 2.0 g (26.8 mol) of KCl in 25 ml of water for two hours, during which the solution changed from a dark red to green. The solution was hot filtered and a greenish-yellow powder formed on cooling. The powder was recrystallized by vapor diffusion of diethylether into a DMF solution of the complex yielding yellow-orange crystals. Infrared spectra were in agreement with literature values (Nakamoto *et al.*, 1965)

Data sets on multiple crystals showed evidence of at least two independent domains, either from agglomeration or from the crystal being cracked or split, perhaps during rapid cooling to 200 K.

Refinement

The matrix relating the two domains, [1.007 0.033 - 0.041 - 0.010 1.013 - 0.022 0.118 0.060 0.975], corresponding to a rotation of 4.4 degrees about the reciprocal axis (-0.351 1.000 0.742), was determined using the *CELL_NOW* program (Bruker AXS, 2009). Integration and absorption correction (TWINABS, Bruker AXS 2009) gave 1558 unique reflections in domain 1, 1560 unique reflections in domain 2, and 211 unique overlapping reflections, or 14 percent overlapping reflections. The structure was solved using merged reflections from both domains (type HKLF 4 in SHELXL-97). The

structure was refined using corrected reflections from only the major component including overlaps (type HKLF 5 in SHELXL-97).

Refinement produced a minor component fraction of 0.084 (6). All hydrogen atoms were positioned geometrically and refined with the atom positions constrained to appropriate positions with N—H distances of 0.91 Å and C—H distances of either 0.95 Å (amide) or 0.98 Å (methyl groups). A riding model was used for all H atoms with $U_{\text{iso}}(\text{H}) = 1.2$ times U_{iso} (amine, amide) or 1.5 times U_{iso} (methyl carbon atoms).

Computing details

Data collection: *APEX2* and *GIS* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009); molecular graphics: *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *POV-RAY* (Cason, 2004); software used to prepare material for publication: *publCIF* (Westrip, 2010).

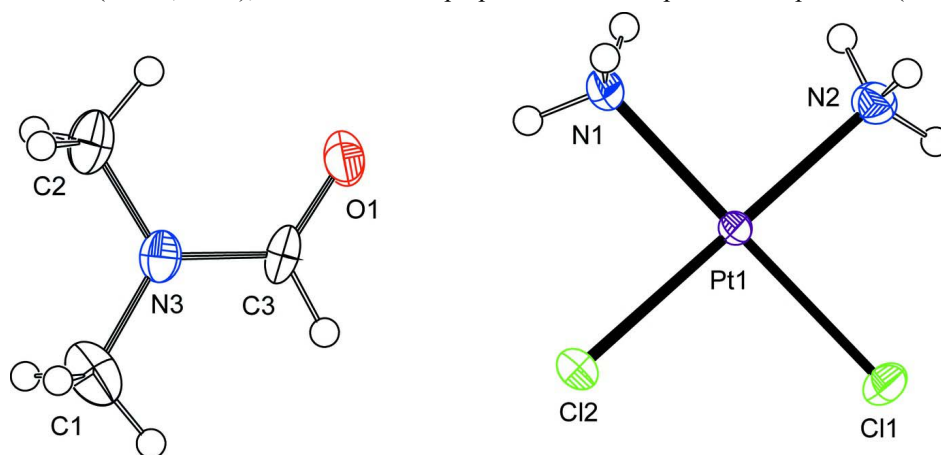
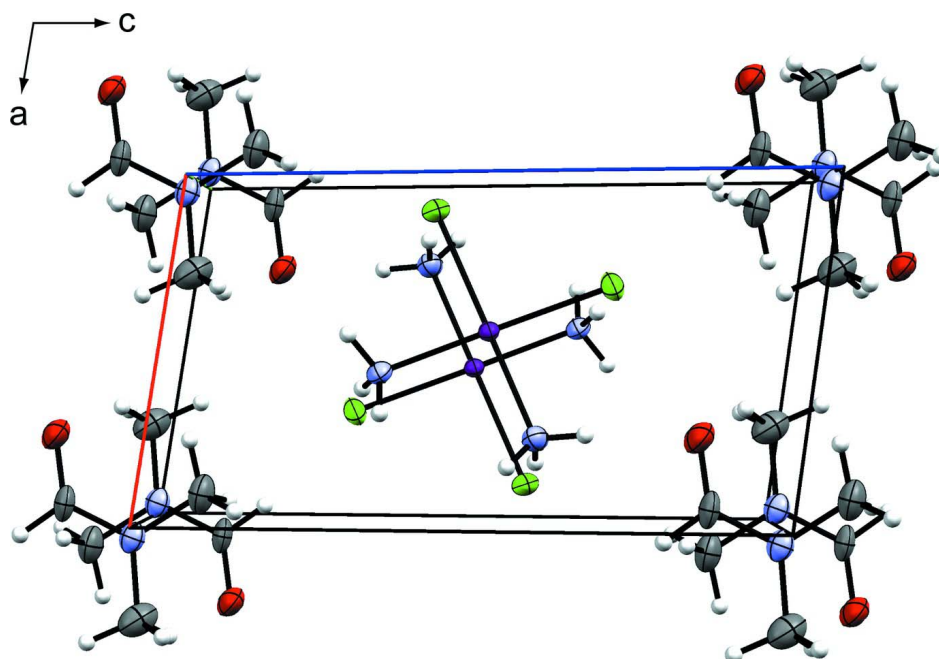
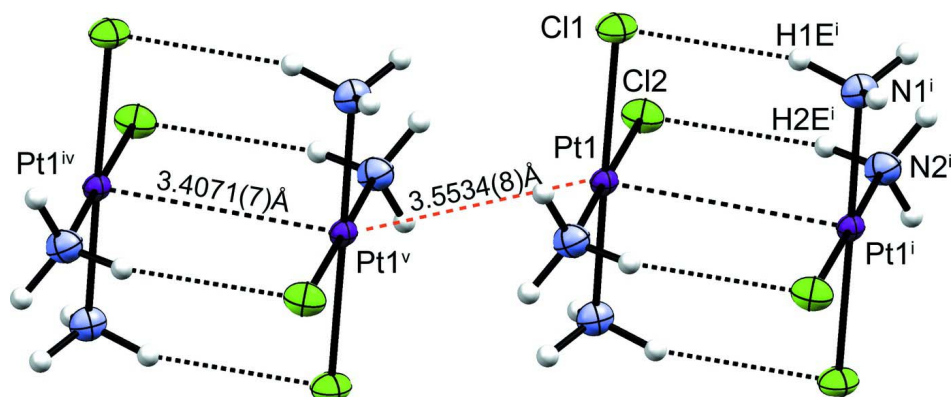


Figure 1

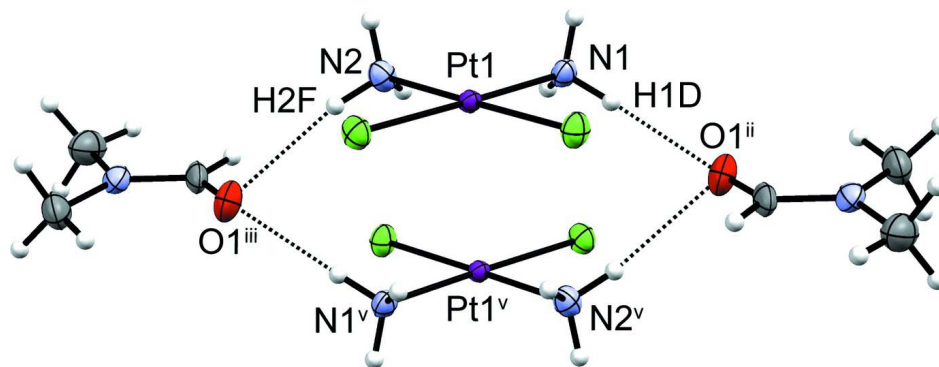
The molecular structure of the title compound drawn with 50% probability displacement ellipsoids for non-H atoms.


Figure 2

The packing of the title compound viewed along the *b* axis drawn with 50% probability displacement ellipsoids for non-H atoms.


Figure 3

A view showing the platinum-platinum interactions and hydrogen bonding between the ammine ligands and the chlorine atoms on neighboring complexes. Additional donor/acceptor distances and angles are listed in Table 1. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (iv) $x, y + 1, z$; (v) $-x + 1, -y + 2, -z + 1$.]


Figure 4

An illustration of the hydrogen bond interactions between the ammine ligands and the *N,N*-dimethylformamide solvent molecules. Additional donor/acceptor distances and angles are listed in Table 1. [Symmetry codes: (ii) $-x + 2, -y + 2, -z + 2$; (iii) $x - 1, y, z - 1$; (v) $-x + 1, -y + 2, -z + 1$.]

cis-Diamminedichloridoplatinum(II) *N,N*-dimethylformamide monosolvate

Crystal data

[PtCl₂(NH₃)₂] \cdot C₃H₇NO

$M_r = 373.15$

Triclinic, $P\bar{1}$

$a = 6.2344$ (9) Å

$b = 6.8196$ (11) Å

$c = 11.5833$ (18) Å

$\alpha = 105.285$ (4) $^\circ$

$\beta = 96.061$ (4) $^\circ$

$\gamma = 97.809$ (4) $^\circ$

$V = 465.47$ (12) Å³

$Z = 2$

$F(000) = 344$

$D_x = 2.662$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1090 reflections

$\theta = 3.3$ – 24.8°

$\mu = 15.59$ mm⁻¹

$T = 200$ K

Plate, clear yellow

$0.46 \times 0.36 \times 0.10$ mm

Data collection

Bruker SMART X2S benchtop
diffractometer

Radiation source: fine-focus sealed tube

Doubly curved silicon crystal monochromator

Detector resolution: 8.3330 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(TWINABS; Bruker, 2009)

$T_{\min} = 0.05, T_{\max} = 0.30$

7440 measured reflections

1620 independent reflections

1484 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 25.1^\circ, \theta_{\min} = 3.1^\circ$

$h = -7 \rightarrow 7$

$k = -8 \rightarrow 7$

$l = 0 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.072$

$S = 1.07$

1620 reflections

96 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)]$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.44$ e Å⁻³

$\Delta\rho_{\min} = -2.08$ e Å⁻³

Special details

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.55286 (4)	0.74780 (4)	0.49265 (2)	0.01388 (13)
Cl1	0.6813 (3)	0.6374 (3)	0.31075 (18)	0.0250 (4)
Cl2	0.8971 (3)	0.7991 (3)	0.60324 (18)	0.0244 (4)
N1	0.4361 (11)	0.8403 (11)	0.6522 (6)	0.0211 (15)
H1D	0.5443	0.9266	0.7089	0.025*
H1E	0.3894	0.7281	0.6772	0.025*
H1F	0.3222	0.9076	0.6419	0.025*
N2	0.2485 (11)	0.6999 (11)	0.3960 (6)	0.0236 (15)
H2D	0.1706	0.7943	0.4345	0.028*
H2E	0.1786	0.5706	0.3897	0.028*
H2F	0.2604	0.7135	0.3208	0.028*
O1	1.2567 (10)	0.8302 (10)	1.1506 (5)	0.0335 (15)
N3	0.9601 (11)	0.7534 (9)	1.0048 (6)	0.0254 (17)
C1	0.7242 (15)	0.7227 (15)	0.9760 (9)	0.041 (2)
H1A	0.6598	0.7511	1.0510	0.061*
H1B	0.6694	0.5797	0.9279	0.061*
H1C	0.6836	0.8165	0.9294	0.061*
C2	1.0852 (17)	0.7125 (15)	0.9063 (8)	0.037 (2)
H2A	1.2411	0.7612	0.9374	0.055*
H2B	1.0389	0.7845	0.8476	0.055*
H2C	1.0608	0.5637	0.8667	0.055*
C3	1.0583 (16)	0.8090 (13)	1.1198 (7)	0.027 (2)
H3	0.9686	0.8339	1.1818	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.01315 (19)	0.01376 (19)	0.01392 (18)	0.00092 (13)	0.00190 (12)	0.00322 (13)
Cl1	0.0266 (11)	0.0290 (11)	0.0192 (10)	0.0044 (9)	0.0089 (8)	0.0044 (8)
Cl2	0.0164 (10)	0.0311 (12)	0.0230 (10)	0.0032 (9)	-0.0005 (8)	0.0049 (9)
N1	0.018 (4)	0.022 (4)	0.019 (3)	-0.001 (3)	0.000 (3)	0.003 (3)
N2	0.020 (4)	0.029 (4)	0.023 (4)	0.005 (3)	0.003 (3)	0.010 (3)
O1	0.030 (4)	0.037 (4)	0.025 (3)	0.005 (3)	-0.005 (3)	-0.001 (3)
N3	0.031 (5)	0.020 (4)	0.022 (4)	0.003 (3)	0.001 (3)	0.003 (3)
C1	0.036 (6)	0.040 (6)	0.045 (6)	-0.001 (5)	-0.007 (5)	0.017 (5)
C2	0.049 (6)	0.038 (6)	0.022 (5)	0.008 (5)	0.001 (4)	0.009 (4)
C3	0.042 (6)	0.023 (5)	0.013 (4)	0.006 (4)	0.001 (4)	0.001 (4)

Geometric parameters (Å, °)

Pt1—N1	2.034 (6)	N3—C3	1.339 (10)
Pt1—N2	2.037 (6)	N3—C2	1.437 (11)
Pt1—C11	2.3088 (19)	N3—C1	1.447 (11)
Pt1—C12	2.313 (2)	C1—H1A	0.9800
N1—H1D	0.9100	C1—H1B	0.9800
N1—H1E	0.9100	C1—H1C	0.9800
N1—H1F	0.9100	C2—H2A	0.9800
N2—H2D	0.9100	C2—H2B	0.9800
N2—H2E	0.9100	C2—H2C	0.9800
N2—H2F	0.9100	C3—H3	0.9500
O1—C3	1.229 (11)		
N1—Pt1—N2	91.8 (3)	C3—N3—C2	120.9 (8)
N1—Pt1—C11	178.99 (19)	C3—N3—C1	120.9 (8)
N2—Pt1—C11	87.6 (2)	C2—N3—C1	118.1 (8)
N1—Pt1—C12	87.9 (2)	N3—C1—H1A	109.5
N2—Pt1—C12	179.34 (18)	N3—C1—H1B	109.5
C11—Pt1—C12	92.63 (7)	H1A—C1—H1B	109.5
Pt1—N1—H1D	109.5	N3—C1—H1C	109.5
Pt1—N1—H1E	109.5	H1A—C1—H1C	109.5
H1D—N1—H1E	109.5	H1B—C1—H1C	109.5
Pt1—N1—H1F	109.5	N3—C2—H2A	109.5
H1D—N1—H1F	109.5	N3—C2—H2B	109.5
H1E—N1—H1F	109.5	H2A—C2—H2B	109.5
Pt1—N2—H2D	109.5	N3—C2—H2C	109.5
Pt1—N2—H2E	109.5	H2A—C2—H2C	109.5
H2D—N2—H2E	109.5	H2B—C2—H2C	109.5
Pt1—N2—H2F	109.5	O1—C3—N3	124.3 (8)
H2D—N2—H2F	109.5	O1—C3—H3	117.8
H2E—N2—H2F	109.5	N3—C3—H3	117.8
C2—N3—C3—O1	0.3 (12)	C1—N3—C3—O1	177.2 (8)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1E...C11 ⁱ	0.91	2.51	3.389 (7)	161
N2—H2E...C12 ⁱ	0.91	2.53	3.403 (7)	162
N1—H1D...O1 ⁱⁱ	0.91	2.13	3.023 (9)	167
N2—H2F...O1 ⁱⁱⁱ	0.91	2.31	3.198 (9)	165

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