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Bis(2-methyl-4-nitroanilinium) tetrachloridomercurate(II)

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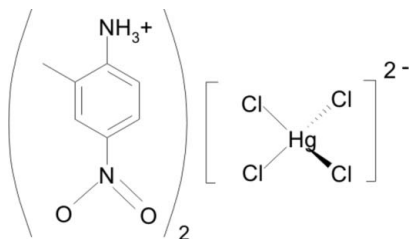
Received 6 November 2008; accepted 18 November 2008

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.053; wR factor = 0.152; data-to-parameter ratio = 24.6.

The title compound, $(\text{C}_7\text{H}_9\text{N}_2\text{O}_2)_2[\text{HgCl}_4]$, self-assembles into cationic organic bilayers containing the 2-methyl-4-nitroanilinium cations, sandwiched between anionic inorganic layers built up by the distorted tetrahedral $[\text{HgCl}_4]^{2-}$ groups. The organic sheets are interlinked through weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, while they interact with the anionic part *via* strong charge-assisted $\text{N}^+-\text{H}\cdots\text{Cl}-\text{Hg}$ hydrogen bonds. The $[\text{HgCl}_4]^{2-}$ anions are bisected by a mirror plane passing through the metal and two of the chloride ions.

Related literature

The structures of bis(2-methyl-4-nitroanilinium) tetrachlorocadmiate (Azumi *et al.*, 1996) as well as those of the bromide and iodide salts of 2-methyl-4-nitroanilinium (Lemmerer & Billing, 2006) have already been reported. For related literature on $\text{C}-\text{H}\cdots\text{O}_{\text{nitro}}$ interactions, see: Sharma & Desiraju (1994).



Experimental

Crystal data

 $(\text{C}_7\text{H}_9\text{N}_2\text{O}_2)_2[\text{HgCl}_4]$ $M_r = 648.71$ Orthorhombic, $Pnma$ $a = 8.2527$ (11) Å $b = 30.059$ (4) Å $c = 8.3038$ (10) Å $V = 2059.9$ (5) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 8.02$ mm⁻¹ $T = 173$ (2) K $0.42 \times 0.25 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: integration (*XPREP*; Bruker, 1999) $T_{\text{min}} = 0.609$, $T_{\text{max}} = 0.757$

10307 measured reflections

3174 independent reflections

2197 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.091$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.053$ $wR(F^2) = 0.152$ $S = 1.09$

3174 reflections

129 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 1.05$ e Å⁻³ $\Delta\rho_{\text{min}} = -2.89$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H6}\cdots\text{Cl2}$	0.91	2.76	3.257 (6)	116
$\text{N1}-\text{H4}\cdots\text{Cl1}^i$	0.91	2.35	3.248 (6)	170
$\text{N1}-\text{H5}\cdots\text{Cl1}^{ii}$	0.91	2.49	3.381 (7)	167
$\text{N1}-\text{H6}\cdots\text{Cl3}^{iii}$	0.91	2.54	3.241 (7)	134
$\text{C3}-\text{H1}\cdots\text{O1}^{iv}$	0.95	2.52	3.424 (10)	160

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

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006) and *Mercury* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2223).

References

- Azumi, R., Honda, K., Goto, M., Akimoto, J., Oosawa, Y., Tachibana, H., Tanaka, M. & Matsumoto, M. (1996). *Acta Cryst.* **C52**, 588–591.
- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SMART-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus* (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Lemmerer, A. & Billing, D. G. (2006). *Acta Cryst.* **C62**, o271–o273.
- Sharma, C. V. K. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 2345–2352.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

Acta Cryst. (2008). E64, m1598 [doi:10.1107/S1600536808038415]

Bis(2-methyl-4-nitroanilinium) tetrachloridomercurate(II)

Jasrotia Dinesh, Melanie Rademeyer, David G. Billing and Andreas Lemmerer

S1. Comment

As part of a study focused on the fundamental understanding of the non-covalent interactions occurring in organic-inorganic hybrids, the structure of bis(2-methyl-4-nitroanilinium) tetrachloromercurate, $2(\text{C}_7\text{H}_9\text{N}_2\text{O}_2)^+(\text{HgCl}_4)^{2-}$, (I), was determined. It was found that the title compound is isostructural to the previously reported hybrid, bis(2-methyl-4-nitroanilinium) tetrachlorocadmate (Azumi *et al.*, 1996). The structures of the bromide and iodide salts of the 2-methyl-4-nitroanilinium cation have already been reported (Lemmerer & Billing, 2006).

The molecular geometry and atomic numbering scheme of (I) are illustrated in Fig. 1. The asymmetric unit contains one 2-methyl-4-nitroanilinium cation and a HgCl_4^{2-} anion, halved by a mirror plane ($x, 1/2-y, z$) passing through the metal and two of the chlorine ions. The structure consists of alternating, non-interdigitated organic bilayers containing the 2-methyl-4-nitroanilinium cations, and inorganic layers containing the isolated $(\text{HgCl}_4)^{2-}$ anions (Fig. 2.).

In the organic bilayers the nitro groups pack in the centre of the layer, in a tail-to-tail arrangement, and the aromatic ring plane (C1->C6) forms an angle of 86.3° to the inorganic layer plane. It has been reported by Sharma and Desiraju (1994) that weak C—H \cdots O interactions, with the nitro group as a hydrogen bond acceptor occurs in many unsaturated compounds, despite the fact that the nitro group is not very basic, and it is precisely this type of interaction the one which links both organic layers in (I): atom C3 on the aromatic ring at symmetry position $(1/2 - x, 1/2 + y, z - 1/2)$ acts as proton donor while the O1 of nitro group at symmetry position $(x, 1/2 - y, z)$ acts as acceptor, with an H \cdots O distance of 2.52 Å.

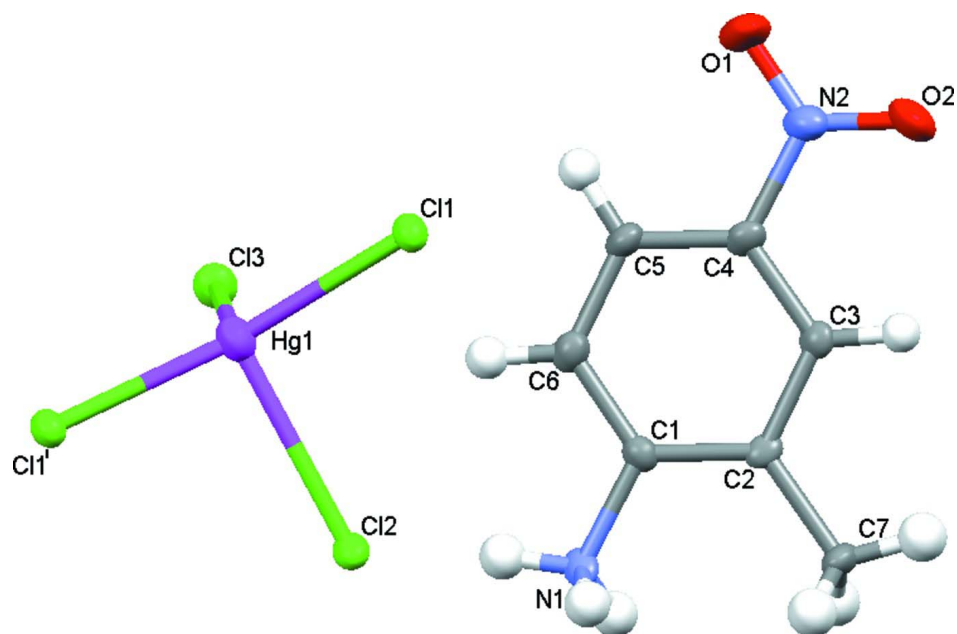
The organic and inorganic layers are linked through charge assisted N $^+$ —H \cdots Cl—Hg hydrogen bonds, with the hydrogen bonding interactions listed in Table 1. N1 is the only hydrogen bond donor with all three hydrogen atoms involved in hydrogen bonding. Atom H6 is shared by two chlorine atoms (Cl2 at symmetry position: (x, y, z) and Cl3 at symmetry position: $(x - 1/2, 1/2 - y, 1/2 - z)$) and thus forms a bifurcated interaction. Two approximately linear hydrogen bonds are formed through atoms H4 and H5 with Cl1 at symmetry positions $(x - 1, y, z)$ and $(x - 1/2, y, 1/2 - z)$, respectively. All four chloro ligands on the HgCl_4^{2-} anion act as hydrogen bond acceptors.

S2. Experimental

Compound (I) was prepared by the addition of 0.097 g (0.357 mmol) of HgCl_2 (Aldrich) and 0.102 g (0.333 mmol) of 2-methyl-4-nitroaniline (Aldrich) to 6 ml of 33% HCl. Complete dissolution was obtained after refluxing at 90°C for 12 h in an oil bath. Slow cooling in oil bath over 48 h produced the crystals. A colourless crystal of $0.42 \times 1/4 \times 0.16$ mm was used for X-ray data collection.

S3. Refinement

H atoms were placed geometrically and refined in idealized positions in the riding-model approximation, with C—H 0.95 (ArH) and 0.98 Å (CH_3) and N—H = 0.91 Å; $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}), 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for other H atoms. The highest residual peaks in the final ΔF syntheses lie at 0.90 Å from Cl3.

**Figure 1**

Atom labelling scheme of (I) with thermal ellipsoids drawn at the 50% probability level. The Cl atom marked with a prime (') is at symmetry position $(1/2 + x, 1/2 - y, 1/2 - z)$.

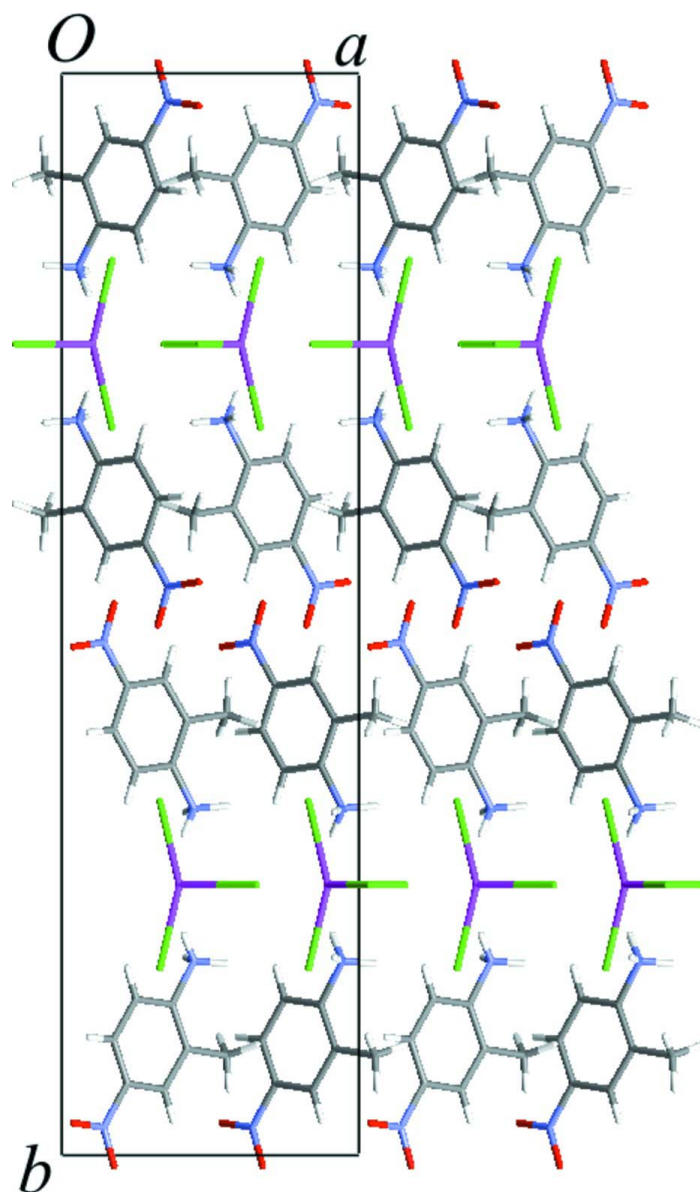


Figure 2

Packing arrangement viewed down the *c*-axis.

Bis(2-methyl-4-nitroanilinium) tetrachloridomercurate(II)

Crystal data

(C₇H₉N₂O₂)₂[HgCl₄]

M_r = 648.71

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

a = 8.2527 (11) Å

b = 30.059 (4) Å

c = 8.3038 (10) Å

V = 2059.9 (5) Å³

Z = 4

F(000) = 1240

D_x = 2.092 Mg m⁻³

Melting point: 441 K

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 937 reflections

θ = 3.2–28.3°

μ = 8.02 mm⁻¹

T = 173 K

Plate, colourless

0.42 × 0.25 × 0.16 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: integration
 (XPREP; Bruker, 1999)
 $T_{\min} = 0.609$, $T_{\max} = 0.757$

10307 measured reflections
 3174 independent reflections
 2197 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.091$
 $\theta_{\max} = 32.2^\circ$, $\theta_{\min} = 1.4^\circ$
 $h = -11 \rightarrow 12$
 $k = -38 \rightarrow 44$
 $l = -8 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.152$
 $S = 1.09$
 3174 reflections
 129 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
 $w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 1.1955P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 1.05 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.89 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. Numerical integration absorption corrections based on indexed crystal faces were applied using the XPREP routine (Bruker, 2004)

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.

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Hg1	0.60393 (5)	0.2500	0.46538 (6)	0.02730 (16)
Cl3	0.4637 (3)	0.2500	0.1888 (3)	0.0232 (5)
Cl1	0.6690 (2)	0.17293 (6)	0.5175 (2)	0.0198 (3)
C1	0.1288 (8)	0.1395 (2)	0.5286 (9)	0.0167 (13)
C6	0.2495 (9)	0.1443 (3)	0.4129 (9)	0.0210 (15)
H3	0.2794	0.1731	0.3760	0.025*
O1	0.4612 (9)	0.0300 (2)	0.2467 (9)	0.0504 (19)
O2	0.3238 (8)	-0.00979 (19)	0.4124 (8)	0.0394 (15)
N1	0.0546 (7)	0.1794 (2)	0.5922 (8)	0.0194 (12)
H6	0.0891	0.2034	0.5347	0.029*
H5	0.0832	0.1828	0.6973	0.029*
H4	-0.0551	0.1772	0.5845	0.029*
C2	0.0779 (7)	0.0982 (2)	0.5872 (8)	0.0151 (13)
N2	0.3592 (7)	0.0258 (2)	0.3538 (8)	0.0252 (14)

C4	0.2790 (8)	0.0663 (3)	0.4125 (8)	0.0189 (14)
C3	0.1558 (8)	0.0608 (2)	0.5265 (8)	0.0171 (13)
H1	0.1257	0.0319	0.5619	0.021*
C5	0.3261 (8)	0.1068 (2)	0.3516 (8)	0.0199 (14)
H2	0.4075	0.1091	0.2711	0.024*
C7	-0.0544 (9)	0.0924 (2)	0.7085 (9)	0.0223 (16)
H9	-0.0626	0.0610	0.7383	0.033*
H8	-0.1575	0.1023	0.6621	0.033*
H7	-0.0299	0.1102	0.8045	0.033*
Cl2	0.3444 (3)	0.2500	0.6670 (3)	0.0199 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0319 (2)	0.0206 (2)	0.0293 (3)	0.000	0.00001 (19)	0.000
Cl3	0.0272 (13)	0.0262 (13)	0.0162 (11)	0.000	-0.0057 (10)	0.000
Cl1	0.0186 (8)	0.0166 (8)	0.0243 (8)	0.0002 (6)	-0.0007 (7)	0.0008 (7)
C1	0.018 (3)	0.016 (3)	0.017 (3)	0.000 (3)	-0.003 (3)	-0.002 (3)
C6	0.022 (3)	0.024 (4)	0.017 (3)	-0.006 (3)	0.000 (3)	-0.001 (3)
O1	0.057 (4)	0.039 (4)	0.055 (4)	-0.007 (4)	0.038 (4)	-0.013 (3)
O2	0.047 (4)	0.020 (3)	0.051 (4)	0.005 (3)	0.012 (3)	-0.007 (3)
N1	0.010 (2)	0.018 (3)	0.030 (3)	-0.001 (2)	-0.003 (2)	0.000 (3)
C2	0.010 (3)	0.023 (4)	0.013 (3)	0.000 (2)	-0.003 (2)	0.001 (3)
N2	0.020 (3)	0.027 (4)	0.030 (4)	0.000 (3)	0.004 (2)	-0.007 (3)
C4	0.019 (3)	0.025 (4)	0.013 (3)	-0.003 (3)	0.001 (3)	-0.004 (3)
C3	0.015 (3)	0.019 (3)	0.017 (3)	-0.004 (3)	-0.003 (3)	-0.002 (3)
C5	0.018 (3)	0.024 (4)	0.018 (3)	-0.004 (3)	0.005 (3)	-0.001 (3)
C7	0.021 (3)	0.022 (4)	0.024 (4)	0.001 (3)	0.010 (3)	0.003 (3)
Cl2	0.0143 (10)	0.0189 (11)	0.0266 (13)	0.000	0.0004 (9)	0.000

Geometric parameters (Å, °)

Hg1—C11	2.4170 (18)	N1—H5	0.9100
Hg1—C11 ⁱ	2.4170 (18)	N1—H4	0.9100
Hg1—Cl3	2.572 (2)	C2—C3	1.390 (10)
Hg1—Cl2	2.718 (2)	C2—C7	1.496 (10)
C1—C6	1.392 (10)	N2—C4	1.469 (10)
C1—C2	1.396 (10)	C4—C5	1.375 (10)
C1—N1	1.447 (9)	C4—C3	1.399 (10)
C6—C5	1.388 (10)	C3—H1	0.9500
C6—H3	0.9500	C5—H2	0.9500
O1—N2	1.230 (9)	C7—H9	0.9800
O2—N2	1.212 (9)	C7—H8	0.9800
N1—H6	0.9100	C7—H7	0.9800
Cl1—Hg1—Cl1 ⁱ	146.85 (9)	C1—C2—C7	123.9 (6)
Cl1—Hg1—Cl3	105.06 (4)	O2—N2—O1	123.0 (7)
Cl1 ⁱ —Hg1—Cl3	105.06 (4)	O2—N2—C4	119.3 (6)

C11—Hg1—C12	93.71 (5)	O1—N2—C4	117.6 (7)
C11 ⁱ —Hg1—C12	93.71 (5)	C5—C4—C3	124.0 (7)
C13—Hg1—C12	101.28 (8)	C5—C4—N2	119.0 (6)
C6—C1—C2	123.2 (7)	C3—C4—N2	117.0 (6)
C6—C1—N1	117.9 (6)	C2—C3—C4	119.0 (7)
C2—C1—N1	118.9 (6)	C2—C3—H1	120.5
C5—C6—C1	119.7 (7)	C4—C3—H1	120.5
C5—C6—H3	120.2	C4—C5—C6	117.1 (6)
C1—C6—H3	120.2	C4—C5—H2	121.5
C1—N1—H6	109.5	C6—C5—H2	121.5
C1—N1—H5	109.5	C2—C7—H9	109.5
H6—N1—H5	109.5	C2—C7—H8	109.5
C1—N1—H4	109.5	H9—C7—H8	109.5
H6—N1—H4	109.5	C2—C7—H7	109.5
H5—N1—H4	109.5	H9—C7—H7	109.5
C3—C2—C1	117.0 (6)	H8—C7—H7	109.5
C3—C2—C7	119.1 (7)		
C2—C1—C6—C5	-0.6 (11)	O1—N2—C4—C3	175.8 (7)
N1—C1—C6—C5	178.6 (6)	C1—C2—C3—C4	0.2 (9)
C6—C1—C2—C3	1.0 (10)	C7—C2—C3—C4	179.7 (7)
N1—C1—C2—C3	-178.1 (6)	C5—C4—C3—C2	-2.1 (11)
C6—C1—C2—C7	-178.4 (7)	N2—C4—C3—C2	179.1 (6)
N1—C1—C2—C7	2.4 (10)	C3—C4—C5—C6	2.5 (11)
O2—N2—C4—C5	176.5 (7)	N2—C4—C5—C6	-178.7 (6)
O1—N2—C4—C5	-3.1 (10)	C1—C6—C5—C4	-1.2 (10)
O2—N2—C4—C3	-4.6 (10)		

Symmetry code: (i) $x, -y+1/2, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H6 \cdots C12	0.91	2.76	3.257 (6)	116
N1—H4 \cdots C11 ⁱⁱ	0.91	2.35	3.248 (6)	170
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