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A second monoclinic polymorph of 2,9-dimethyl-1,10-phenanthroline dihydrate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.062
wR factor = 0.154
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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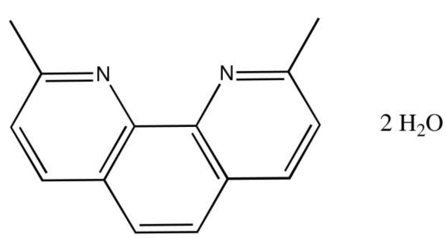
A second monoclinic polymorph of the title compound, neocuproine dihydrate, $C_{14}H_{12}N_2\cdot2H_2O$, is reported. Unlike the first polymorph [Baggio, Baggio & Mombrú (1998). *Acta Cryst.* C**54**, 1900–1902], in which the phenanthroline ring system was constrained to lie in a crystallographic mirror plane, here there is no such imposed symmetry. Consequently, the molecule shows small deviations from planarity, the outer rings being twisted slightly in opposite directions from the plane of the central ring. The hydrogen-bonding motifs remain essentially the same as in the first polymorph, involving small rings of four water molecules and large rings containing four water molecules and two neocuproine molecules, but with no H-atom disorder for the water molecules in this case. There are also aromatic π–π stacking interactions.

Comment

In our ongoing research on squaric acid, we have synthesized some mixed-ligand metal complexes of squaric acid and their structures have been reported (Uçar *et al.*, 2004, 2005; Bulut *et al.*, 2004). We have used such co-ligands as isonicotinamide and 2,9-dimethyl-1,10-phenanthrolione (neocuproine) in our research and, while synthesizing an iron complex of squaric acid and neocuproine, we obtained crystals of neocuproine dihydrate, (I), as a side product. A unit cell search of the Cambridge Structural Database (CSD, Version 5.26 plus three updates; Allen, 2002) did not find a match, and it was only by carrying out a structure-based search that we found that a structure of the same compound, also as a dihydrate, had previously been reported (Baggio *et al.*, 1998). The crystal structure of a hemihydrate has also been determined (Britton *et al.*, 1991). A unit-cell determination with our sample at 298 K gave essentially the same parameters as were determined at 150 K, with the expected slight expansion, and so we are confident that we are reporting the crystal structure of a second monoclinic polymorph of (I), and not the result of a phase transition at low temperature.



(I)

This second monoclinic polymorph of (I), shown in Fig. 1, crystallizes in space group $C2/c$ with all atoms lying in general

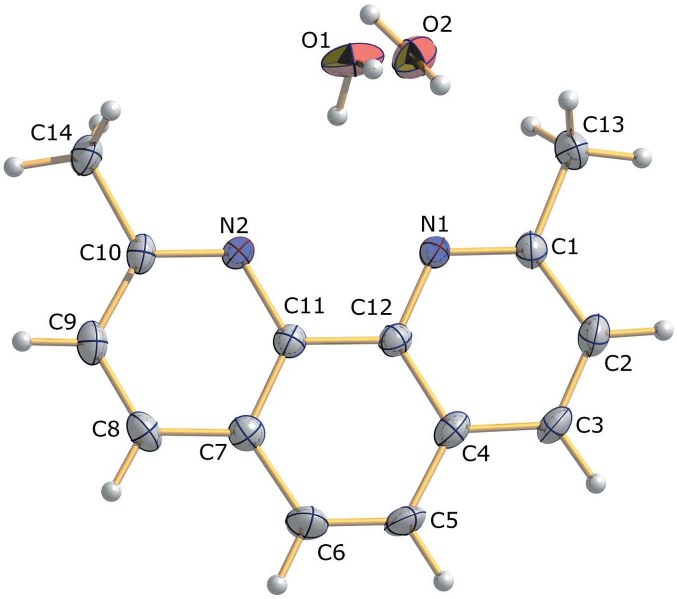


Figure 1
The asymmetric unit of compound (I), with displacement ellipsoids drawn at the 50% probability level.

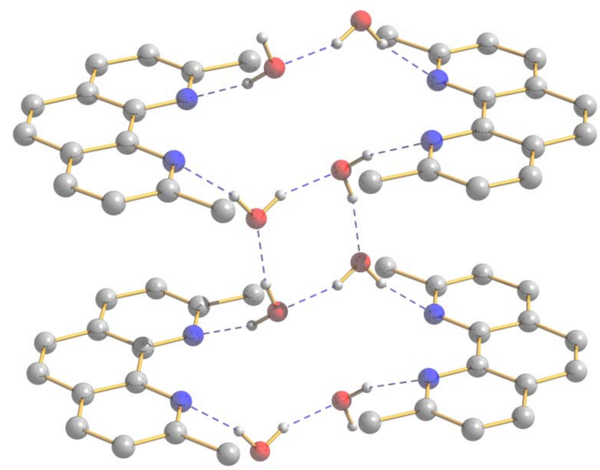


Figure 2
The hydrogen-bonding motifs in (I). Dashed lines indicate the hydrogen bonds.

positions. Britton *et al.* (1991) reported some slight tilting of the individual six-membered rings with respect to one another within the phenanthroline system in the hemihydrate. Baggio *et al.* (1998) reported that the molecule was exactly planar in the first polymorph of the dihydrate, as a consequence of crystallographic mirror symmetry. A least-squares plane fitted through all non-H atoms of the phenathroline skeleton of (I) has an r.m.s. deviation of 0.024 Å, and the dihedral angle between two mean planes fitted through the outermost rings is 2.37 (2)°, indicating a small deviation of the molecule from planarity. This distortion consists mainly of a twist of the outer rings in opposite directions out of the plane of the central ring, as indicated by the N1—C12—C11—N2 torsion angle of −2.8 (3)°, almost the same as the above dihedral angle.

The overall crystal packing of (I) is similar to that in the first monoclinic polymorph, albeit without the perfectly planar sheets achieved by imposed mirror symmetry. In the first polymorph, H-atom disorder in the water molecules means there is more than one possible orientation of each water molecule and hence some uncertainty about the hydrogen-bonding arrangement. In (I), all H atoms were easily and convincingly located in a difference map and water H atoms were freely refined. The hydrogen-bonding arrangement is shown in Fig. 2. The water molecules form hydrogen bonds around an inversion centre to generate a square $R_4^4(8)$ motif (Bernstein *et al.*, 1995). A second large $R_6^6(18)$ motif links two neocuproine molecules together *via* the water molecules.

Unlike the first polymorph, we find no evidence of weak C—H···O hydrogen bonding here. However, the separations between parallel neocuproine molecules stacked along the *b* axis are alternately 3.32 and 3.39 Å, and each molecule has approximately a half-ring overlap with the next molecule in the stack, characteristic of aromatic π–π interactions.

Experimental

Squaric acid, H_2Sq (0.57 g, 5 mmol) dissolved in water (25 ml) was neutralized with NaOH (0.40 g, 10 mmol) and the mixture was added to a hot solution of $FeCl_2\cdot6H_2O$ (1.17 g, 5 mmol) dissolved in water (50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The brown crystals that formed were filtered off, washed with water and ethanol, and dried *in vacuo*. A solution of 2,9-dimethyl-1,10-phenanthroline (0.435 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of $FeSq\cdot2H_2O$ (0.21 g, 1 mmol) in water (50 ml). The brown solution was refluxed for about 2 h and then cooled to room temperature. A few days later, brown crystals of the desired Fe complex had formed, along with some well formed colourless crystals of (I) as a side-product.

Crystal data

$C_{14}H_{12}N_2\cdot2H_2O$
$M_r = 244.29$
Monoclinic, $C2/c$
$a = 22.942$ (2) Å
$b = 6.7388$ (7) Å
$c = 17.9594$ (18) Å
$\beta = 116.019$ (2)°
$V = 2495.2$ (4) Å^3
$Z = 8$
$D_x = 1.301$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6879 reflections
$\theta = 2.4$–28.8°
$\mu = 0.09$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.61 × 0.38 × 0.21 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Thin–slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.928$, $T_{max} = 0.982$
8619 measured reflections
2191 independent reflections
1781 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.0$°
$h = -27 \rightarrow 27$
$k = -7 \rightarrow 8$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.154$
$S = 1.22$
2191 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 4.5458P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N2	0.84 (4)	2.31 (4)	3.105 (3)	157 (3)
O1—H2O···O2	0.87 (5)	1.95 (5)	2.805 (3)	167 (4)
O2—H3O···N1^{i}	0.88 (4)	2.15 (4)	3.005 (3)	164 (3)
O2—H4O···O1^{ii}	0.89 (3)	1.97 (3)	2.810 (3)	158 (3)

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

All H atoms were located in a difference Fourier map. Water H atoms were freely refined, giving O—H distances shown in Table 1. Other H atoms were treated as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.95 Å for aromatic, and $U_{iso}(H) = 1.5U_{eq}(C)$ and C—H = 0.98 Å for methyl groups.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXTL* and local programs.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Baggio, S., Baggio, R. & Mombrú, A. W. (1998). *Acta Cryst.* C**54**, 1900–1902.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Brandenburg, K. & Putz, H. (2004). *DIAMOND*. Version 3. University of Bonn, Germany.
Britton, D., Thompson, L. C. & Holz, R. C. (1991). *Acta Cryst.* C**47**, 1101–1103.
Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bulut, A., Uçar, I., Yeşilel, O. Z., Içbudak, H., Ölmez, H. & Büyükgüngör, O. (2004). *Acta Cryst.* C**60**, m526–m528.
Sheldrick, G. M. (2001). *SHELXTL*. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Uçar, I., Bulut, A. & Büyükgüngör, O. (2005). *Acta Cryst.* C**61**, m218–m220.
Uçar, I., Yeşilel, O. Z., Bulut, A., Ölmez, H. & Büyükgüngör, O. (2004). *Acta Cryst.* E**60**, m1025–m1027.

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$C_{14}H_{12}N_2\cdot 2H_2O$
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Monoclinic, $C2/c$
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$V = 2495.2$ (4) Å^3
$Z = 8$
$F(000) = 1040$
$D_x = 1.301$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
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1781 reflections with $I > 2\sigma(I)$
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$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
$h = -27 \rightarrow 27$
$k = -7 \rightarrow 8$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.154$
$S = 1.22$
2191 reflections
181 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 4.5458P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.19573 (11)	0.4772 (4)	−0.01527 (15)	0.0406 (6)
H1O	0.1883 (16)	0.553 (6)	0.017 (2)	0.055 (11)*
H2O	0.1861 (18)	0.355 (7)	−0.009 (2)	0.073 (13)*
O2	0.17540 (10)	0.0684 (3)	−0.00899 (12)	0.0335 (5)
H3O	0.1572 (17)	−0.035 (6)	0.002 (2)	0.055 (11)*
H4O	0.2143 (16)	0.022 (5)	0.0011 (18)	0.038 (9)*
N1	0.08861 (9)	0.7549 (3)	0.00743 (12)	0.0206 (5)
N2	0.20798 (9)	0.7166 (3)	0.13865 (12)	0.0190 (5)
C1	0.03091 (11)	0.7632 (4)	−0.05702 (15)	0.0239 (6)
C2	−0.02721 (12)	0.7565 (4)	−0.04881 (16)	0.0299 (6)
H2	−0.0678	0.7609	−0.0966	0.036*
C3	−0.02506 (12)	0.7436 (4)	0.02798 (16)	0.0283 (6)
H3	−0.0640	0.7420	0.0344	0.034*
C4	0.03580 (11)	0.7325 (4)	0.09819 (16)	0.0243 (6)
C5	0.04243 (12)	0.7185 (4)	0.18106 (16)	0.0301 (6)
H5	0.0046	0.7160	0.1901	0.036*
C6	0.10114 (13)	0.7087 (4)	0.24644 (16)	0.0301 (6)
H6	0.1042	0.7012	0.3009	0.036*
C7	0.15925 (12)	0.7094 (4)	0.23481 (15)	0.0225 (6)
C8	0.22152 (12)	0.6992 (4)	0.30111 (15)	0.0256 (6)
H8	0.2268	0.6918	0.3565	0.031*
C9	0.27443 (12)	0.6998 (4)	0.28505 (16)	0.0254 (6)
H9	0.3168	0.6953	0.3295	0.030*
C10	0.26627 (11)	0.7072 (3)	0.20277 (15)	0.0204 (5)
C11	0.15525 (11)	0.7208 (3)	0.15433 (14)	0.0191 (5)
C12	0.09161 (11)	0.7366 (3)	0.08391 (14)	0.0200 (5)
C13	0.03040 (12)	0.7823 (5)	−0.14102 (15)	0.0337 (7)
H13A	0.0561	0.8982	−0.1414	0.051*
H13B	−0.0143	0.7986	−0.1835	0.051*
H13C	0.0491	0.6625	−0.1528	0.051*
C14	0.32325 (11)	0.7054 (4)	0.18304 (16)	0.0272 (6)
H14A	0.3246	0.5786	0.1571	0.041*
H14B	0.3633	0.7221	0.2342	0.041*
H14C	0.3191	0.8142	0.1448	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0556 (14)	0.0307 (12)	0.0565 (14)	0.0088 (10)	0.0440 (12)	0.0049 (11)
O2	0.0324 (11)	0.0283 (11)	0.0437 (12)	−0.0050 (9)	0.0204 (10)	−0.0016 (9)
N1	0.0164 (10)	0.0252 (12)	0.0200 (10)	0.0002 (8)	0.0077 (8)	0.0009 (9)
N2	0.0163 (10)	0.0201 (10)	0.0213 (10)	−0.0004 (8)	0.0089 (8)	0.0001 (8)
C1	0.0195 (12)	0.0268 (14)	0.0220 (13)	−0.0010 (10)	0.0060 (10)	−0.0026 (11)
C2	0.0177 (12)	0.0373 (16)	0.0288 (14)	−0.0011 (11)	0.0049 (11)	−0.0027 (12)
C3	0.0150 (12)	0.0370 (16)	0.0348 (15)	−0.0011 (11)	0.0125 (11)	−0.0017 (12)

C4	0.0183 (12)	0.0257 (14)	0.0306 (14)	0.0015 (10)	0.0121 (11)	0.0009 (11)
C5	0.0234 (13)	0.0441 (16)	0.0309 (14)	0.0015 (12)	0.0192 (12)	0.0031 (13)
C6	0.0317 (14)	0.0395 (16)	0.0239 (13)	−0.0008 (12)	0.0166 (12)	0.0041 (12)
C7	0.0248 (13)	0.0202 (13)	0.0224 (13)	−0.0009 (10)	0.0103 (10)	0.0014 (10)
C8	0.0299 (14)	0.0262 (14)	0.0169 (12)	−0.0012 (11)	0.0068 (11)	−0.0001 (10)
C9	0.0199 (12)	0.0245 (13)	0.0247 (13)	0.0003 (10)	0.0032 (10)	0.0008 (11)
C10	0.0154 (12)	0.0173 (12)	0.0234 (13)	0.0000 (9)	0.0039 (10)	0.0002 (10)
C11	0.0187 (12)	0.0163 (12)	0.0219 (12)	0.0003 (10)	0.0085 (10)	−0.0005 (10)
C12	0.0199 (12)	0.0188 (12)	0.0222 (12)	−0.0008 (10)	0.0100 (10)	−0.0007 (10)
C13	0.0242 (13)	0.0524 (18)	0.0207 (13)	−0.0001 (13)	0.0064 (11)	−0.0009 (13)
C14	0.0166 (12)	0.0334 (15)	0.0279 (14)	0.0022 (11)	0.0064 (11)	0.0012 (12)

Geometric parameters (Å, º)

O1—H1O	0.84 (4)	C5—C6	1.345 (4)
O1—H2O	0.87 (5)	C6—H6	0.950
O2—H3O	0.88 (4)	C6—C7	1.437 (3)
O2—H4O	0.89 (3)	C7—C8	1.404 (3)
N1—C1	1.323 (3)	C7—C11	1.410 (3)
N1—C12	1.350 (3)	C8—H8	0.950
N2—C10	1.329 (3)	C8—C9	1.365 (4)
N2—C11	1.357 (3)	C9—H9	0.950
C1—C2	1.405 (4)	C9—C10	1.407 (3)
C1—C13	1.509 (3)	C10—C14	1.497 (3)
C2—H2	0.950	C11—C12	1.457 (3)
C2—C3	1.361 (4)	C13—H13A	0.980
C3—H3	0.950	C13—H13B	0.980
C3—C4	1.414 (3)	C13—H13C	0.980
C4—C5	1.431 (4)	C14—H14A	0.980
C4—C12	1.412 (3)	C14—H14B	0.980
C5—H5	0.950	C14—H14C	0.980
H1O—O1—H2O	110 (3)	C7—C8—C9	119.3 (2)
H3O—O2—H4O	102 (3)	H8—C8—C9	120.4
C1—N1—C12	118.6 (2)	C8—C9—H9	120.0
C10—N2—C11	118.1 (2)	C8—C9—C10	120.1 (2)
N1—C1—C2	122.5 (2)	H9—C9—C10	120.0
N1—C1—C13	116.4 (2)	N2—C10—C9	122.1 (2)
C2—C1—C13	121.1 (2)	N2—C10—C14	116.5 (2)
C1—C2—H2	120.2	C9—C10—C14	121.4 (2)
C1—C2—C3	119.6 (2)	N2—C11—C7	123.3 (2)
H2—C2—C3	120.2	N2—C11—C12	117.8 (2)
C2—C3—H3	120.3	C7—C11—C12	118.9 (2)
C2—C3—C4	119.3 (2)	N1—C12—C4	122.7 (2)
H3—C3—C4	120.3	N1—C12—C11	118.3 (2)
C3—C4—C5	122.9 (2)	C4—C12—C11	119.0 (2)
C3—C4—C12	117.1 (2)	C1—C13—H13A	109.5
C5—C4—C12	119.9 (2)	C1—C13—H13B	109.5

C4—C5—H5	119.3	C1—C13—H13C	109.5
C4—C5—C6	121.3 (2)	H13A—C13—H13B	109.5
H5—C5—C6	119.3	H13A—C13—H13C	109.5
C5—C6—H6	119.6	H13B—C13—H13C	109.5
C5—C6—C7	120.7 (2)	C10—C14—H14A	109.5
H6—C6—C7	119.6	C10—C14—H14B	109.5
C6—C7—C8	122.7 (2)	C10—C14—H14C	109.5
C6—C7—C11	120.1 (2)	H14A—C14—H14B	109.5
C8—C7—C11	117.2 (2)	H14A—C14—H14C	109.5
C7—C8—H8	120.4	H14B—C14—H14C	109.5

C12—N1—C1—C2	0.9 (4)	C8—C9—C10—C14	−179.2 (2)
C12—N1—C1—C13	−179.6 (2)	C10—N2—C11—C7	−2.0 (3)
N1—C1—C2—C3	0.9 (4)	C10—N2—C11—C12	178.3 (2)
C13—C1—C2—C3	−178.6 (3)	C6—C7—C11—N2	−178.1 (2)
C1—C2—C3—C4	−1.4 (4)	C6—C7—C11—C12	1.5 (3)
C2—C3—C4—C5	−179.9 (3)	C8—C7—C11—N2	1.9 (4)
C2—C3—C4—C12	0.3 (4)	C8—C7—C11—C12	−178.5 (2)
C3—C4—C5—C6	−179.8 (3)	C1—N1—C12—C4	−2.1 (3)
C12—C4—C5—C6	−0.1 (4)	C1—N1—C12—C11	178.0 (2)
C4—C5—C6—C7	−0.8 (4)	C3—C4—C12—N1	1.5 (4)
C5—C6—C7—C8	−179.9 (3)	C3—C4—C12—C11	−178.5 (2)
C5—C6—C7—C11	0.1 (4)	C5—C4—C12—N1	−178.2 (2)
C6—C7—C8—C9	179.7 (2)	C5—C4—C12—C11	1.7 (4)
C11—C7—C8—C9	−0.3 (4)	N2—C11—C12—N1	−2.8 (3)
C7—C8—C9—C10	−1.1 (4)	N2—C11—C12—C4	177.3 (2)
C11—N2—C10—C9	0.6 (3)	C7—C11—C12—N1	177.6 (2)
C11—N2—C10—C14	−179.3 (2)	C7—C11—C12—C4	−2.4 (3)
C8—C9—C10—N2	1.0 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···N2	0.84 (4)	2.31 (4)	3.105 (3)	157 (3)
O1—H2*O*···O2	0.87 (5)	1.95 (5)	2.805 (3)	167 (4)
O2—H3*O*···N1^{i}	0.88 (4)	2.15 (4)	3.005 (3)	164 (3)
O2—H4*O*···O1^{ii}	0.89 (3)	1.97 (3)	2.810 (3)	158 (3)

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