

Pyridinium *trans*-diaquabis[oxalato(2-)- κ^2O^1,O^2]chromate(III) urea monosolvate

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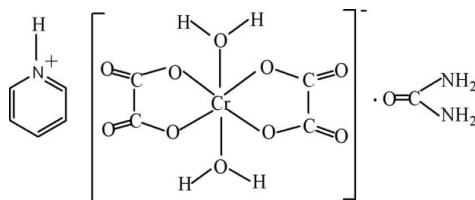
Received 17 September 2013; accepted 21 September 2013

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.041; wR factor = 0.111; data-to-parameter ratio = 17.8.

The asymmetric unit of the title solvated molecular salt, $(C_5H_6N)[Cr(C_2O_4)_2(H_2O)_2] \cdot CO(NH_2)_2$, contains half a formula unit. Each component is completed by crystallographic twofold symmetry: in the cation, one C and the N atom lie on the rotation axis; in the anion, the Cr^{III} ion lies on the axis; in the solvent molecule, the C and the O atom lie on the axis. The aqua ligands are in a *trans* disposition in the resulting CrO₆ octahedron. In the crystal, the components are linked by O—H...O, N—H...O and N—H...O(O) hydrogen bonds, generating a three-dimensional network.

Related literature

For molecular salts containing the $[Cr(C_2O_4)_2(H_2O)_2]^-$ anion, see: Bélombé *et al.* (2009); Nenwa *et al.* (2010, 2012); Chérif *et al.* (2011); Chérif, Zid *et al.* (2012); Chérif, Abdelhak *et al.* (2012); Dridi *et al.* (2013).



Experimental

Crystal data

$(C_5H_6N)[Cr(C_2O_4)_2(H_2O)_2] \cdot CH_4N_2O$

$M_r = 404.24$

Monoclinic, $I2/a$

$a = 7.6456$ (7) Å

$b = 21.4096$ (18) Å

$c = 9.7404$ (12) Å

$\beta = 100.278$ (1)°

$V = 1568.8$ (3) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.80$ mm⁻¹

$T = 293$ K

$0.20 \times 0.16 \times 0.13$ mm

Data collection

Bruker APEX CCD diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2004)

$T_{\min} = 0.851$, $T_{\max} = 0.935$

11770 measured reflections

2343 independent reflections

1980 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.111$

$S = 1.10$

2343 reflections

132 parameters

5 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.30$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.56$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cr4—O2	1.9436 (12)	Cr4—O1	1.9955 (14)
Cr4—O3	1.9762 (12)		

Table 2

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—H1...O4 ⁱ	0.86	2.26	2.979 (3)	142
N1—H1...O4 ⁱⁱ	0.86	2.26	2.979 (3)	142
N2—H2A...O4 ⁱⁱⁱ	0.82 (2)	2.36 (2)	3.134 (2)	158 (3)
N2—H2B...O5 ^{iv}	0.79 (2)	2.08 (2)	2.847 (2)	166 (3)
O1—H1B...O3 ⁱⁱⁱ	0.81 (2)	1.91 (2)	2.7135 (18)	174 (3)
O1—H1A...O6	0.81 (2)	1.79 (2)	2.5910 (16)	176 (3)

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

The authors thank Tobias Storp (RWTH Aachen) for his technical support during the X-ray experiments.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7141).

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supporting information

Acta Cryst. (2013). E69, m567 [doi:10.1107/S1600536813026135]

Pyridinium *trans*-diaquabis[oxalato(2-)- κ^2O^1,O^2]chromate(III) urea monosolvate

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S1. Comment

Recently, the crystal structures of some salts involving organic cations and the complex anion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$, have been reported (Bélombé *et al.*, 2009; Nenwa *et al.*, 2010; Chérif, Zid *et al.*, 2012; Chérif, Abdelhak *et al.*, 2012; Nenwa, Gouet *et al.* 2012). We now report the structure of the title compound, with the organic cation, pyridinium, the *trans*-diaquabis(oxalato)chromate(III) complex anion and the urea molecule which replaces the fraction of water molecule of crystallization in the previously described structures (Chérif *et al.*, 2011; Chérif, Abdelhak *et al.*, 2012; Dridi *et al.*, 2013).

The constituents of the title compound are shown in Fig.1. It appears to be the first member of salts with general formula $A_m[M(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot x\text{OC}(\text{NH}_2)_2$; where A = organic cation, M = metal(II) or metal(III), m = 1 or 2 and $x \geq 0$. The asymmetric unit is formed by a pyridinium cation, a $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ anionic complex in *trans*-aqua configuration and one urea molecule. The chromium (III) ion lies on a twofold axis and is six-coordinated in a distorted octahedral geometry defined by four O atoms from two chelating bidentate oxalate anions in the equatorial plane and by two O atoms from two apical aqua ligands. The equatorial Cr–O_(oxalate) distances, 1.9435 (13) Å and 1.9762 (13) Å, are slightly shorter than the axial Cr–O_(water) one [1.9955 (15) Å]. These bond distances are similar to those observed in homologous complex salts (Bélombé *et al.*, 2009; Nenwa *et al.*, 2010; Chérif *et al.*, 2011; Chérif, Abdelhak *et al.*, 2012; Chérif, Abdelhak *et al.*, 2012; Nenwa *et al.*, 2012; Dridi *et al.*, 2013).

The crystal structure can be described by a characteristic layered arrangement of the pyridinium cation, $(\text{C}_5\text{H}_6\text{N})^+$, the complex anion, $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$, and the urea molecule (Fig. 2). O–H \cdots O and N–H \cdots O hydrogen bonding interactions link the components (Fig.3).

S2. Experimental

1 mmol (267 mg) of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 ml of water. The green filtered solution was stirred at 323 K, 2 mmol (253 mg) of oxalic acid, 1 mmol (79.1 mg) of pyridine and 2 mmol (121 mg) of urea were added in successive small portions and stirred for 2 h. The resulting violet solution was left at room temperature; violet prisms were obtained after one week of slow evaporation.

S3. Refinement

The H atoms of the pyridinium cation were positioned geometrically, with C–H, N–H distances of 0.93 and 0.86 Å respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The urea H atoms were located in a difference Fourier map and freely refined.

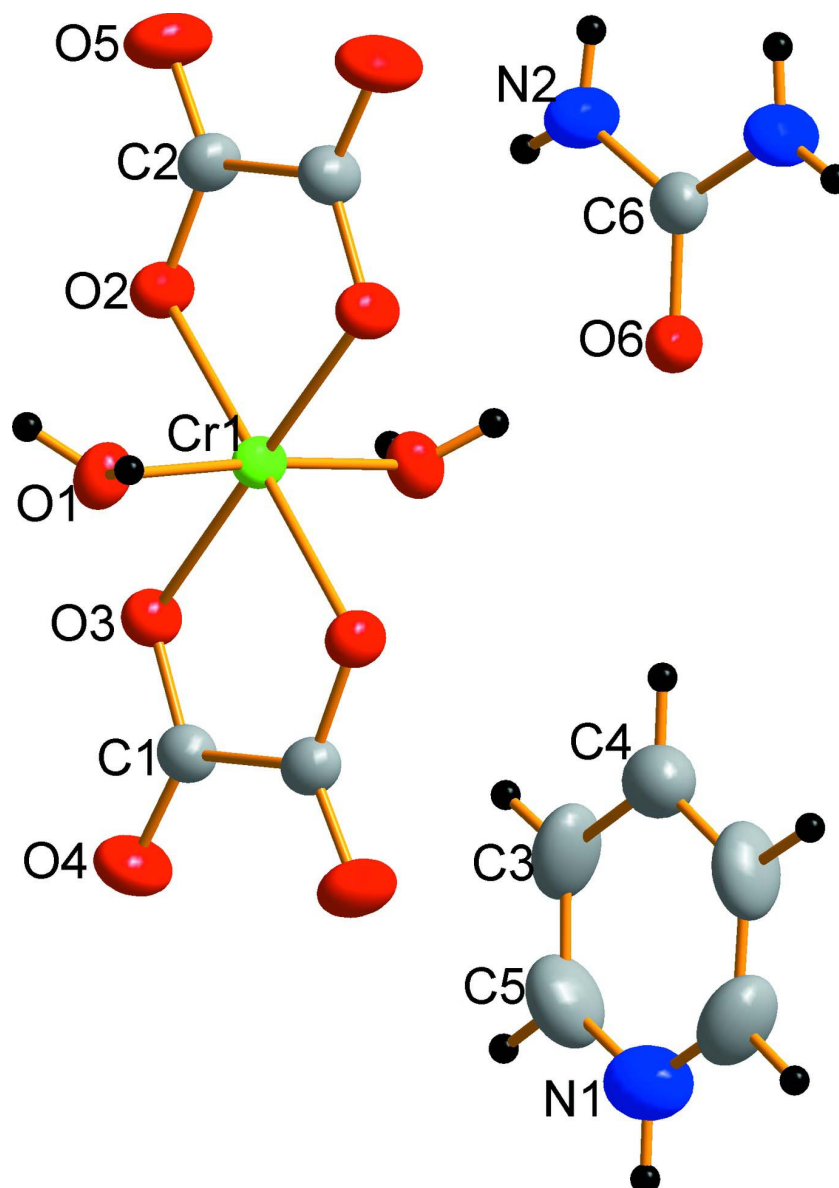


Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

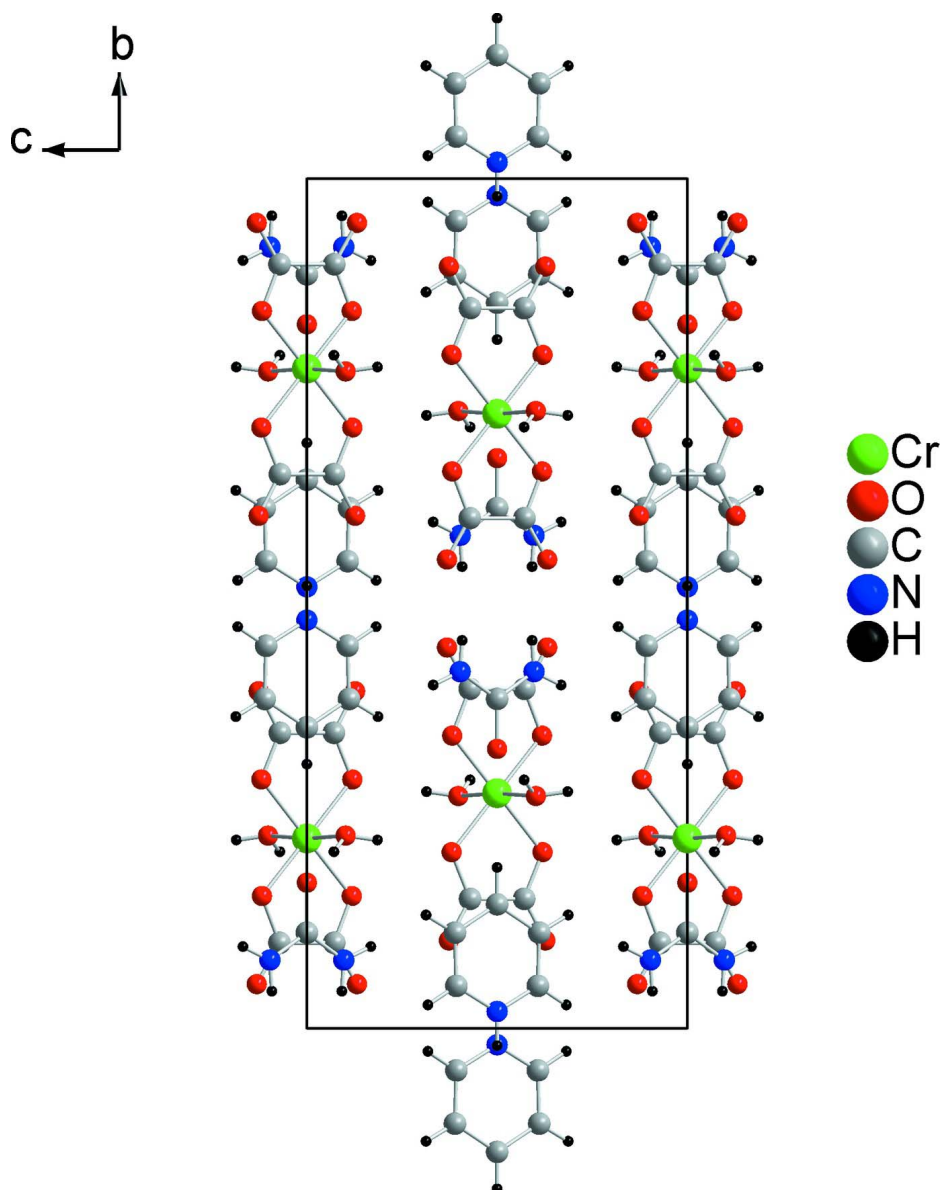


Figure 2

Packing diagram of the title compound, viewed along the *a* axis, showing its layered structure.

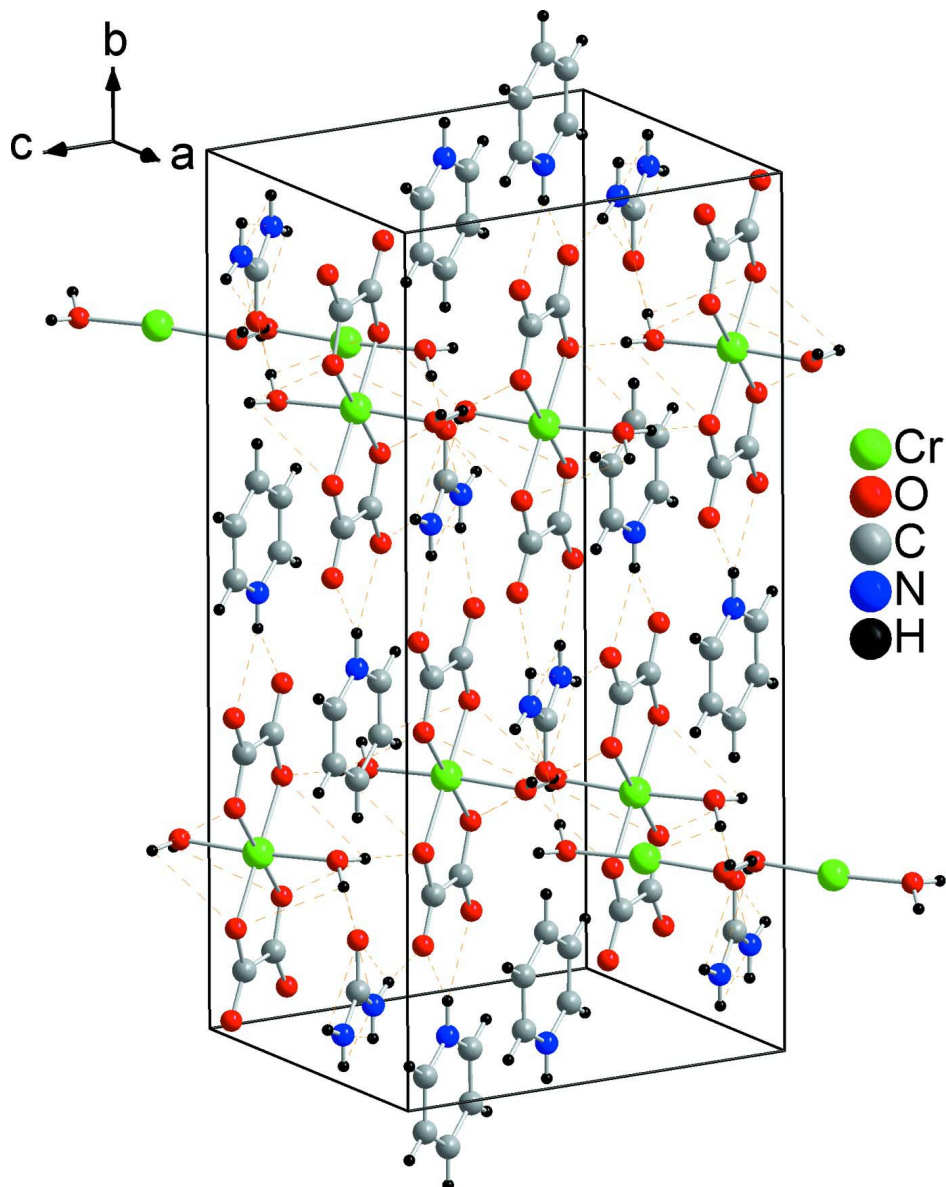


Figure 3

Interconnection of the constituents of the title compound into a three-dimensional network. Hydrogen bonds are highlighted with dashed lines.

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Crystal data

$(C_5H_6N)[Cr(C_2O_4)_2(H_2O)_2] \cdot CH_4N_2O$

$M_r = 404.24$

Monoclinic, $I2/a$

Hall symbol: $-I 2/a$

$a = 7.6456 (7) \text{ \AA}$

$b = 21.4096 (18) \text{ \AA}$

$c = 9.7404 (12) \text{ \AA}$

$\beta = 100.278 (1)^\circ$

$V = 1568.8 (3) \text{ \AA}^3$

$Z = 4$

$F(000) = 828$

$D_x = 1.712 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

$\mu = 0.80 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism, violet

$0.20 \times 0.16 \times 0.13 \text{ mm}$

Data collection

Bruker APEX CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2004)
 $T_{\min} = 0.851$, $T_{\max} = 0.935$

11770 measured reflections
2343 independent reflections
1980 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 30.9^\circ$, $\theta_{\min} = 2.3^\circ$
 $h = -10 \rightarrow 10$
 $k = -30 \rightarrow 30$
 $l = -13 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.111$
 $S = 1.10$
2343 reflections
132 parameters
5 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 1.3542P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.56 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr4	0.2500	0.223340 (17)	0.0000	0.02410 (13)
O1	0.45417 (19)	0.22672 (6)	-0.10198 (14)	0.0315 (3)
O2	0.35892 (18)	0.15558 (6)	0.11799 (13)	0.0324 (3)
O3	0.14209 (17)	0.29281 (6)	-0.11952 (12)	0.0288 (3)
O4	0.1309 (2)	0.39675 (7)	-0.12681 (15)	0.0436 (4)
O5	0.3604 (2)	0.05182 (7)	0.13176 (16)	0.0498 (4)
C1	0.1842 (2)	0.34777 (8)	-0.07105 (17)	0.0285 (3)
C2	0.3134 (3)	0.10049 (8)	0.07197 (18)	0.0319 (4)
N1	0.7500	0.48039 (15)	0.0000	0.0622 (8)
H1	0.7500	0.5206	0.0000	0.075*
C3	0.8444 (3)	0.38759 (15)	0.1108 (3)	0.0576 (7)
H3	0.9099	0.3668	0.1868	0.069*
C4	0.7500	0.35421 (17)	0.0000	0.0527 (8)
H4	0.7500	0.3108	0.0000	0.063*
C5	0.8402 (4)	0.45021 (15)	0.1071 (3)	0.0594 (7)

H5	0.9023	0.4727	0.1819	0.071*
O6	0.7500	0.17120 (9)	0.0000	0.0388 (4)
N2	0.6418 (3)	0.08022 (9)	-0.0971 (2)	0.0447 (4)
C6	0.7500	0.11234 (13)	0.0000	0.0326 (5)
H2A	0.584 (3)	0.0960 (12)	-0.168 (2)	0.055 (8)*
H2B	0.649 (4)	0.0435 (8)	-0.092 (3)	0.061 (9)*
H1B	0.434 (3)	0.2215 (11)	-0.1855 (17)	0.049 (8)*
H1A	0.544 (3)	0.2077 (11)	-0.071 (2)	0.053 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr4	0.0280 (2)	0.0240 (2)	0.01765 (18)	0.000	-0.00312 (13)	0.000
O1	0.0307 (7)	0.0389 (7)	0.0229 (6)	0.0050 (5)	-0.0004 (5)	-0.0009 (5)
O2	0.0385 (7)	0.0280 (6)	0.0259 (6)	0.0010 (5)	-0.0071 (5)	0.0020 (5)
O3	0.0334 (6)	0.0290 (6)	0.0213 (5)	0.0013 (5)	-0.0020 (5)	0.0010 (4)
O4	0.0565 (9)	0.0310 (7)	0.0391 (8)	0.0071 (6)	-0.0026 (7)	0.0067 (6)
O5	0.0713 (11)	0.0278 (7)	0.0433 (8)	0.0053 (7)	-0.0084 (8)	0.0046 (6)
C1	0.0313 (9)	0.0293 (8)	0.0245 (8)	0.0015 (6)	0.0043 (6)	0.0013 (6)
C2	0.0358 (9)	0.0303 (8)	0.0272 (8)	0.0024 (7)	-0.0014 (7)	0.0024 (6)
N1	0.069 (2)	0.0486 (17)	0.071 (2)	0.000	0.0156 (17)	0.000
C3	0.0445 (13)	0.0814 (19)	0.0409 (12)	0.0074 (12)	-0.0084 (10)	0.0166 (12)
C4	0.0477 (19)	0.0471 (18)	0.062 (2)	0.000	0.0057 (16)	0.000
C5	0.0567 (15)	0.0726 (18)	0.0456 (13)	-0.0166 (13)	0.0001 (11)	-0.0139 (12)
O6	0.0303 (9)	0.0295 (9)	0.0514 (12)	0.000	-0.0067 (8)	0.000
N2	0.0520 (11)	0.0336 (9)	0.0434 (10)	-0.0022 (8)	-0.0052 (8)	-0.0043 (8)
C6	0.0291 (12)	0.0338 (12)	0.0346 (12)	0.000	0.0052 (10)	0.000

Geometric parameters (Å, °)

Cr4—O2 ⁱ	1.9436 (12)	N1—C5 ⁱⁱ	1.313 (3)
Cr4—O2	1.9436 (12)	N1—C5	1.313 (3)
Cr4—O3 ⁱ	1.9762 (12)	N1—H1	0.8600
Cr4—O3	1.9762 (12)	C3—C5	1.341 (4)
Cr4—O1	1.9955 (14)	C3—C4	1.385 (3)
Cr4—O1 ⁱ	1.9955 (14)	C3—H3	0.9300
O1—H1B	0.808 (16)	C4—C3 ⁱⁱ	1.385 (3)
O1—H1A	0.808 (16)	C4—H4	0.9300
O2—C2	1.287 (2)	C5—H5	0.9300
O3—C1	1.287 (2)	O6—C6	1.260 (3)
O4—C1	1.217 (2)	N2—C6	1.331 (2)
O5—C2	1.216 (2)	N2—H2A	0.821 (17)
C1—C1 ⁱ	1.559 (3)	N2—H2B	0.788 (17)
C2—C2 ⁱ	1.556 (3)	C6—N2 ⁱⁱ	1.331 (2)
O2 ⁱ —Cr4—O2	83.43 (7)	O3—C1—C1 ⁱ	113.91 (9)
O2 ⁱ —Cr4—O3 ⁱ	179.29 (5)	O5—C2—O2	125.43 (17)
O2—Cr4—O3 ⁱ	97.10 (5)	O5—C2—C2 ⁱ	120.99 (11)

O2 ⁱ —Cr4—O3	97.10 (5)	O2—C2—C2 ⁱ	113.59 (9)
O2—Cr4—O3	179.29 (5)	C5 ⁱⁱ —N1—C5	121.0 (4)
O3 ⁱ —Cr4—O3	82.36 (7)	C5 ⁱⁱ —N1—H1	119.5
O2 ⁱ —Cr4—O1	91.34 (6)	C5—N1—H1	119.5
O2—Cr4—O1	91.76 (6)	C5—C3—C4	119.2 (2)
O3 ⁱ —Cr4—O1	89.11 (5)	C5—C3—H3	120.4
O3—Cr4—O1	87.76 (5)	C4—C3—H3	120.4
O2 ⁱ —Cr4—O1 ⁱ	91.76 (6)	C3—C4—C3 ⁱⁱ	117.9 (4)
O2—Cr4—O1 ⁱ	91.34 (6)	C3—C4—H4	121.1
O3 ⁱ —Cr4—O1 ⁱ	87.76 (5)	C3 ⁱⁱ —C4—H4	121.1
O3—Cr4—O1 ⁱ	89.11 (5)	N1—C5—C3	121.3 (3)
O1—Cr4—O1 ⁱ	175.84 (8)	N1—C5—H5	119.3
Cr4—O1—H1B	117.8 (19)	C3—C5—H5	119.3
Cr4—O1—H1A	119.1 (19)	C6—N2—H2A	124 (2)
H1B—O1—H1A	108 (2)	C6—N2—H2B	116 (2)
C2—O2—Cr4	114.66 (11)	H2A—N2—H2B	119 (3)
C1—O3—Cr4	114.90 (10)	O6—C6—N2	121.10 (13)
O4—C1—O3	125.58 (16)	O6—C6—N2 ⁱⁱ	121.10 (13)
O4—C1—C1 ⁱ	120.51 (11)	N2—C6—N2 ⁱⁱ	117.8 (3)

Symmetry codes: (i) $-x+1/2, y, -z$; (ii) $-x+3/2, y, -z$.

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

<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—H1 \cdots O4 ⁱⁱⁱ	0.86	2.26	2.979 (3)	142
N1—H1 \cdots O4 ^{iv}	0.86	2.26	2.979 (3)	142
N2—H2A \cdots O4 ^v	0.82 (2)	2.36 (2)	3.134 (2)	158 (3)
N2—H2B \cdots O5 ^{vi}	0.79 (2)	2.08 (2)	2.847 (2)	166 (3)
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Symmetry codes: (iii) $-x+1, -y+1, -z$; (iv) $x+1/2, -y+1, z$; (v) $-x+1/2, -y+1/2, -z-1/2$; (vi) $-x+1, -y, -z$.