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# Crystal structure of $[\text{UO}_2(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$

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Pentaammine dioxide uranium(V) nitrate ammonia (1/1),  $[\text{UO}_2(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$ , was obtained in the form of yellow crystals from the reaction of caesium uranyl nitrate,  $\text{Cs}[\text{UO}_2(\text{NO}_3)_3]$ , and uranium tetrafluoride,  $\text{UF}_4$ , in dry liquid ammonia. The  $[\text{UO}_2]^+$  cation is coordinated by five ammine ligands. The resulting  $[\text{UO}_2(\text{NH}_3)_5]$  coordination polyhedron is best described as a pentagonal bipyramid with the O atoms forming the apices. In the crystal, numerous  $\text{N}-\text{H} \cdots \text{N}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds are present between the cation, anion and solvent molecules, leading to a three-dimensional network.

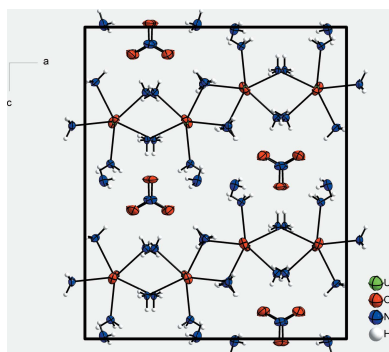
## 1. Introduction – Chemical context

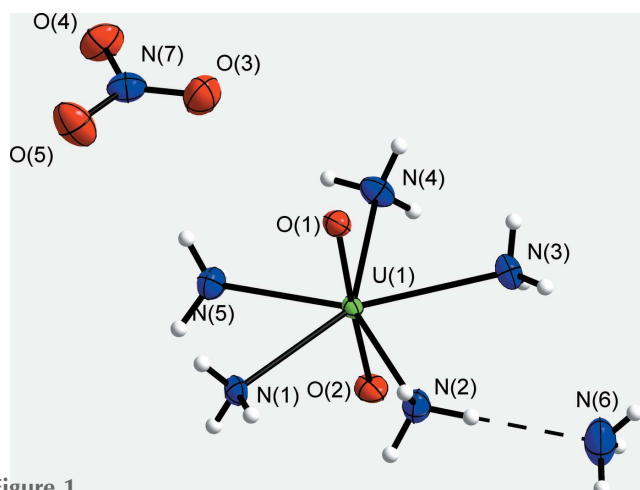
Uranium chemistry in aqueous solution is dominated by the uranyl cation  $[\text{UO}_2]^{2+}$ , with the uranium atom in the hexavalent oxidation state. The most prominent representatives are the well-known uranyl nitrates and uranyl halides. In contrast to the  $[\text{UO}_2]^{2+}$  uranyl cation, the uranyl cation  $[\text{UO}_2]^+$  with pentavalent uranium disproportionates in aqueous solution into the  $[\text{U}^{\text{VI}}\text{O}_2]^{2+}$  cation and a tetravalent uranium species. Only under controlled conditions (Kraus *et al.*, 1949) and in organic solvents (Arnold *et al.*, 2009) are uranyl cations with pentavalent uranium observable. Here we report on the crystal structure of a  $\text{U}^{\text{V}}$  compound,  $[\text{UO}_2(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$ , obtained from the reaction of  $\text{U}^{\text{IV}}$  with  $\text{U}^{\text{VI}}$  species in anhydrous liquid ammonia. The compound is not stable at temperatures above *ca* 238 K due to the loss of ammonia of a still unknown amount. Despite several efforts, we have not yet been able to reproduce the synthesis of the compound.

Obviously, the two uranium compounds used as educts reacted in a comproportionation reaction in order to form the  $\text{U}^{\text{V}}$  compound reported here. It is possible that the redox potentials in liquid ammonia are reversed compared to aqueous solutions, leading to a comproportionation. Such changes of electrochemical potentials are not uncommon and, for example, are known for the system  $\text{Cu}/\text{Cu}^+/\text{Cu}^{2+}$  (Woidy *et al.*, 2015a). However, the detailed reaction  $\text{U}^{\text{VI}} + \text{U}^{\text{IV}} \rightarrow \text{U}^{\text{V}}$  is still unclear, and despite some efforts we were not able to elucidate further reaction products which must be present (*e.g.* fluoride containing ones).

## 2. Results and discussion – Structural commentary

All atoms in the structure of the title compound reside on general Wyckoff positions 8c of space group *Pbca*. The pentavalent uranium atom U1 and the oxygen atoms O1 and O2 form an uranyl cation. This  $[\text{UO}_2]^+$  ion is coordinated by five ammine ligands (N1–N5) forming the complex pentagonal-bipyramidal  $[\text{UO}_2(\text{NH}_3)_5]^+$  cation which is shown in




**Figure 1**

The molecular components of the title compound. Displacement ellipsoids are shown at the 70% probability level. The dashed line corresponds to a N—H···N hydrogen-bonding interaction.

Fig. 1. The nitrate anion  $\text{NO}_3^-$  consists of the nitrogen atom N7 and the oxygen atoms O3–O5. An ammonia molecule of crystallization (N6) is also observed in the structure.

The U—O distances in the almost linear uranyl cation [O—U—O angle of  $177.2(1)^\circ$ ] are  $1.861(3)$  and  $1.867(3)$  Å, respectively. Such distances are slightly elongated compared to reported ones for uranyl compounds with pentavalent uranium (Berthet *et al.*, 2003; Hayton & Wu, 2008), which are in the range  $1.810(4)$  to  $1.828(4)$  Å. However, U—O distances for uranyl cations  $[\text{UO}_2]^{2+}$  with hexavalent uranium are about  $0.02$  to  $0.07$  Å shorter. For the alkali metal uranyl nitrates, such as  $M[\text{UO}_2(\text{NO}_3)_3]$  with  $M = \text{K}$  (Jouffret *et al.*, 2011; Krivovichev & Burns, 2004), Rb (Barclay *et al.*, 1965; Zalkin *et al.*, 1989) and Cs (Malcic & Ljubica, 1961), the reported U—O distances are in the range  $1.746$  to  $1.795$  Å. In uranium(VI) compounds that contain the comparable pentaammine dioxido uranium(VI) ion  $[\text{UO}_2(\text{NH}_3)_5]^{2+}$ , such as  $[\text{UO}_2(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{NH}_3$ ,  $[\text{UO}_2\text{F}_2(\text{NH}_3)_3]_2 \cdot 2\text{NH}_3$  or  $[\text{UO}_2(\text{NH}_3)_5]\text{Br}_2 \cdot \text{NH}_3$ , U—O distances in the range  $1.768(2)$  to  $1.771(3)$  Å were reported (Woidy *et al.*, 2012, 2015b); these are shortened by *ca*  $0.1$  Å compared to the uranyl ion presented here.

The nitrogen atoms of the ammine ligands show U—N distances between  $2.573(3)$  and  $2.629(3)$  Å, which appear slightly elongated in comparison with the U—N distances determined for  $\text{U}^{\text{VI}}$  compounds such as  $[\text{UO}_2(\text{NH}_3)_5]\text{Cl}_2 \cdot \text{NH}_3$  [ $2.505(2)$ – $2.554(3)$  Å],  $[\text{UO}_2(\text{NH}_3)_5]\text{Br}_2 \cdot \text{NH}_3$  or  $[\text{UO}_2\text{F}_2(\text{NH}_3)_3]_2 \cdot 2\text{NH}_3$  [ $2.522(3)$  to  $2.577(3)$  Å] (Woidy *et al.*, 2012). In  $[\text{UF}_4(\text{NH}_3)_4] \cdot \text{NH}_3$  (Kraus & Baer, 2009), we observed an elongated U—N distance of  $2.618(5)$  Å due to the higher coordination number and different charge of the central atom.

The nitrate anion features no unexpected structural parameters and is practically identical compared to the nitrate anions of  $\text{NaNO}_3$  or  $\text{KNO}_3$ . The N—O distances are  $1.242(5)$ ,  $1.253(4)$ , and  $1.254(4)$  Å, the bond angles are  $120^\circ$  within the  $3\sigma$  criterion [ $120.4(3)$ ,  $120.4(3)$ , and  $119.2(3)^\circ$ ] and therefore the anion is essentially planar.

**Table 1**

Hydrogen-bond geometry (Å, °).

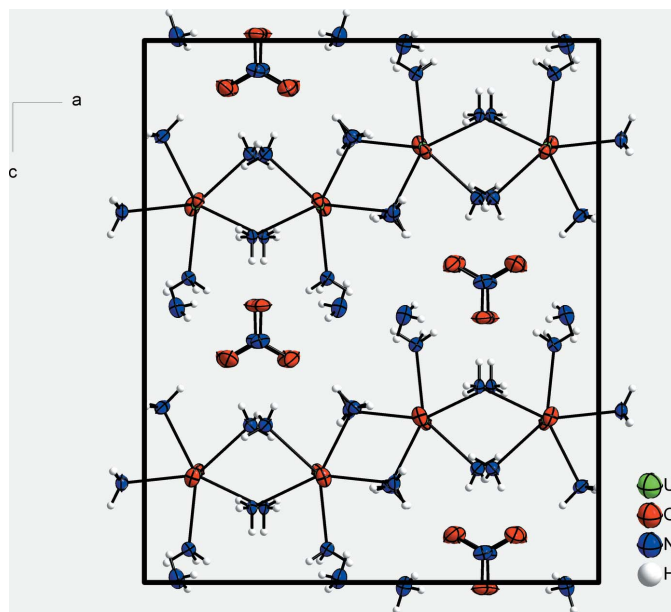
D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O4 <sup>i</sup>	0.91	2.43	3.166 (4)	138
N1—H1A···O4 <sup>ii</sup>	0.91	2.47	2.996 (4)	117
N1—H1B···O1 <sup>iii</sup>	0.91	2.25	3.079 (4)	151
N1—H1C···O2 <sup>iv</sup>	0.91	2.12	3.006 (4)	165
N2—H2A···O4 <sup>i</sup>	0.91	2.49	3.220 (5)	138
N2—H2B···N6	0.91	2.14	3.024 (5)	164
N2—H2C···O4 <sup>ii</sup>	0.91	2.36	3.232 (5)	160
N3—H3A···O2 <sup>v</sup>	0.91	2.27	3.136 (5)	159
N3—H3B···O1 <sup>vi</sup>	0.91	2.34	3.151 (4)	149
N3—H3C···O5 <sup>vii</sup>	0.91	2.52	3.142 (5)	126
N4—H4A···O1 <sup>iii</sup>	0.91	2.37	3.219 (4)	156
N4—H4B···O2 <sup>v</sup>	0.91	2.26	3.086 (4)	150
N4—H4C···O3	0.91	2.55	3.253 (5)	134
N5—H5A···O5 <sup>iii</sup>	0.91	2.14	3.048 (5)	176
N5—H5B···O3	0.91	2.44	3.063 (5)	126
N5—H5B···O5	0.91	2.59	3.394 (5)	147
N5—H5C···O1 <sup>iii</sup>	0.91	2.37	3.273 (4)	171
N6—H6A···O4 <sup>vii</sup>	0.86 (7)	2.50 (7)	3.342 (6)	167 (7)
N6—H6B···O3 <sup>vi</sup>	0.81 (8)	2.32 (8)	3.102 (6)	162 (7)

Symmetry codes: (i)  $-x + \frac{1}{2}, -y, z + \frac{1}{2}$ ; (ii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (v)  $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vi)  $-x, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (vii)  $x - \frac{1}{2}, y, -z + \frac{3}{2}$ .

As we are not able to completely explain the formation of the title compound from the educts, the question arises whether the cation is not simply a ‘regular’ uranyl(VI) cation. It is obvious that no second nitrate anion is present in the structure. Due to chemical reasoning, the ammonia molecule of crystallization also cannot be an amide anion ( $\text{NH}_2^-$ ). As ammine ligands are bound to the uranium cation, some of their electron density is transferred to the Lewis-acidic U atom, which leads to a weakening of the N—H bonds and therefore to an acidification of these protons. So, an amide anion residing next to an acidified ammine ligand is not a plausible assumption, especially since the ammonia molecule of crystallization shows a usual N···N distance for N—H···N hydrogen bonds. If one assumes that  $\text{CO}_3^{2-}$  is present instead of  $\text{NO}_3^-$ , then a ‘regular’  $[\text{U}^{\text{VI}}\text{O}_2]^{2+}$  ion would also result. However, if one refines the occupancy of the N atom of the nitrate anion, an occupancy of  $1.00(2)$  is observed, whereas if the occupancy of the C atom of a putative carbonate anion is refined, an occupancy of  $1.30(2)$  is obtained. Comparing the atomic distances of the trigonal-planar anion with the mean distances from the literature,  $1.284$  Å for  $\text{CO}_3^{2-}$  (Zemann, 1981) and  $1.250$  Å for  $\text{NO}_3^-$  (Baur, 1981), it is most likely that in our case a nitrate anion is present. In summary, all these points indicate that the central atom is an N atom of a nitrate anion. Together with the observation of slightly elongated U—O and U—N bond lengths in comparison to similar  $[\text{UO}_2(\text{NH}_3)_5]^{2+}$  ions, we conclude that the compound should contain  $\text{U}^{\text{V}}$  atoms in form of  $[\text{UO}_2]^+$  ions.

### 3. Supramolecular features

The crystal structure of the title compound is shown in Fig. 2. The ammonia molecule of crystallization (N6) acts as an acceptor of an N—H hydrogen bond with an ammine ligand (N2). It forms also two disparate N—H···O hydrogen bonds



**Figure 2**  
Crystal structure of  $[\text{UO}_2(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$  viewed along  $[010]$ . Displacement ellipsoids are shown at the 70% probability level.

to two symmetry-equivalent nitrate anions; the third H atom (H6C) is not involved in hydrogen-bond formation. The nitrate anion is hydrogen-bonded to five symmetry-related  $[\text{UO}_2(\text{NH}_3)_5]^+$  cations via  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds and two symmetry-related ammonia molecules of crystallization. The nitrate anions lie parallel to the  $ac$  plane and are arranged in columns running parallel to the  $b$  axis (Fig. 2). The oxygen atoms of the uranyl cation act as acceptors of hydrogen bonds from four (O1) and three (O2) ammine ligands of two symmetry-related  $[\text{UO}_2(\text{NH}_3)_5]^+$  cations. The linear  $\text{UO}_2^+$  cations are also arranged parallel to the  $b$  axis. Overall, a three-dimensional hydrogen-bonded network results. Numerical details of the hydrogen bonding interactions are compiled in Table 1.

#### 4. Synthesis and crystallization

The purity of the used educts was evidenced by powder X-ray diffraction and IR spectroscopy. 50 mg (0.09 mmol, 1 eq.)  $\text{Cs}[\text{UO}_2(\text{NO}_3)_3]$  and 27 mg (0.09 mmol, 1 eq.)  $\text{UF}_4$  were placed in a reaction flask under argon atmosphere. After cooling to 195 K ca 10 ml  $\text{NH}_3$  were added to the reaction mixture resulting in a clear yellow solution and a green solid residue. Yellow single crystals of the title compound were obtained during storage at 233 K and were selected under cold perfluoroether oil (Kottke & Stalke, 1993). Additionally, emerald green crystals of  $[\text{UF}_4(\text{NH}_3)_4] \cdot \text{NH}_3$  were observed (Kraus & Baer, 2009) next to colourless crystals of  $\text{CsNO}_3$ , both evidenced by determination of their unit-cell parameters.

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was solved by the

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$[\text{U}(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$
$M_r$	434.24
Crystal system, space group	Orthorhombic, $Pbca$
Temperature (K)	123
$a, b, c$ (Å)	15.7497 (2), 7.7375 (1), 18.8126 (2)
$V$ (Å <sup>3</sup> )	2292.57 (5)
$Z$	8
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	14.17
Crystal size (mm)	0.24 × 0.21 × 0.04
Data collection	
Diffractometer	Oxford Diffraction Xcalibur3
Absorption correction	Multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2009)
$T_{\min}, T_{\max}$	0.166, 1.000
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	88079, 6635, 5051
$R_{\text{int}}$	0.045
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.892
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.090, 1.04
No. of reflections	6635
No. of parameters	136
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	5.60, -3.79

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXL97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *SHELXLX* (Hübschle *et al.*, 2011), *DIAMOND* (Brandenburg, 2012) and *pubCIF* (Westrip, 2010).

heavy-atom method and all other atoms were located from difference Fourier maps. In case of the hydrogen atoms of nitrogen atoms N1–N5, their positions were refined using a riding model with  $\text{N}-\text{H} = 0.91$  Å and  $U_{\text{eq}}(\text{H}) = 1.5U_{\text{iso}}(\text{N})$ . The hydrogen atoms of the ammonia molecule of crystallization were refined freely. The maximum and minimum residual electron densities are located close to the U atom at distances of 0.58 and 0.04 Å, respectively.

#### Acknowledgements

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## supporting information

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Crystal structure of  $[\text{UO}_2(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$ 

Patrick Woidy and Florian Kraus

## Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXL97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## Pentaammine dioxide uranium(V) nitrate ammonia monosolvate

## Crystal data

$[\text{U}(\text{NH}_3)_5]\text{NO}_3 \cdot \text{NH}_3$   
 $M_r = 434.24$   
 Orthorhombic, *Pbcn*  
 $a = 15.7497$  (2) Å  
 $b = 7.7375$  (1) Å  
 $c = 18.8126$  (2) Å  
 $V = 2292.57$  (5) Å<sup>3</sup>  
 $Z = 8$   
 $F(000) = 1592$

$D_x = 2.516$  Mg m<sup>-3</sup>  
 Melting point: not measured K  
 Mo *K*α radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 44787 reflections  
 $\theta = 2.8\text{--}39.2^\circ$   
 $\mu = 14.17$  mm<sup>-1</sup>  
 $T = 123$  K  
 Plate, colourless  
 0.24 × 0.21 × 0.04 mm

## Data collection

Oxford Diffraction Xcalibur3  
 diffractometer  
 Radiation source: Enhance (Mo) X-ray Source  
 Graphite monochromator  
 Detector resolution: 16.0238 pixels mm<sup>-1</sup>  
 phi- and ω-rotation scans  
 Absorption correction: multi-scan  
 (*CrysAlis RED*; Oxford Diffraction, 2009)  
 $T_{\min} = 0.166$ ,  $T_{\max} = 1.000$

88079 measured reflections  
 6635 independent reflections  
 5051 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.045$   
 $\theta_{\max} = 39.3^\circ$ ,  $\theta_{\min} = 3.1^\circ$   
 $h = -27 \rightarrow 27$   
 $k = -8 \rightarrow 13$   
 $l = -32 \rightarrow 32$

## Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.090$   
 $S = 1.04$   
 6635 reflections  
 136 parameters  
 0 restraints  
 Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier map  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 3.9914P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.003$   
 $\Delta\rho_{\max} = 5.60$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -3.79$  e Å<sup>-3</sup>

Extinction correction: SHELXL2014  
 (Sheldrick, 2015),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.00070 (7)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
U1	0.11450 (2)	0.22849 (2)	0.80178 (2)	0.00916 (4)
O1	0.11836 (14)	-0.0112 (4)	0.79457 (13)	0.0145 (4)
O2	0.10583 (16)	0.4688 (4)	0.80629 (15)	0.0180 (5)
N1	0.26344 (17)	0.2174 (4)	0.86194 (16)	0.0140 (5)
H1A	0.257174	0.197530	0.909327	0.021*
H1B	0.290520	0.320039	0.855278	0.021*
H1C	0.294646	0.130809	0.842227	0.021*
N2	0.0977 (2)	0.2180 (5)	0.93878 (17)	0.0182 (6)
H2A	0.111922	0.110928	0.954839	0.027*
H2B	0.042857	0.241370	0.950589	0.027*
H2C	0.132433	0.298114	0.959019	0.027*
N3	-0.04957 (19)	0.2180 (4)	0.81645 (19)	0.0185 (6)
H3A	-0.070849	0.128341	0.790693	0.028*
H3B	-0.072525	0.318832	0.800654	0.028*
H3C	-0.062761	0.203054	0.863146	0.028*
N4	0.0394 (2)	0.2335 (4)	0.67697 (19)	0.0188 (6)
H4A	0.003321	0.325238	0.674759	0.028*
H4B	0.009622	0.133855	0.670795	0.028*
H4C	0.079243	0.243219	0.642176	0.028*
N5	0.2334 (2)	0.2756 (5)	0.70995 (18)	0.0190 (6)
H5A	0.214265	0.346174	0.674728	0.029*
H5B	0.248928	0.172025	0.691072	0.029*
H5C	0.278944	0.325155	0.731585	0.029*
N6	-0.0713 (3)	0.3021 (8)	1.0069 (3)	0.0327 (9)
H6A	-0.110 (4)	0.227 (8)	1.013 (4)	0.033 (19)*
H6B	-0.095 (4)	0.381 (10)	0.986 (4)	0.05 (2)*
H6C	-0.056 (6)	0.312 (12)	1.037 (5)	0.06 (3)*
N7	0.2550 (2)	0.0309 (4)	0.55493 (17)	0.0204 (6)
O3	0.1861 (2)	0.0340 (5)	0.58716 (17)	0.0320 (7)
O4	0.25705 (19)	0.0485 (4)	0.48871 (15)	0.0266 (6)
O5	0.3231 (2)	0.0085 (5)	0.58813 (17)	0.0311 (7)



Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
U1	0.00711 (5)	0.00894 (6)	0.01145 (5)	0.00013 (3)	-0.00104 (3)	-0.00027 (3)
O1	0.0137 (10)	0.0142 (12)	0.0157 (11)	-0.0007 (8)	-0.0016 (8)	-0.0011 (8)
O2	0.0176 (11)	0.0096 (11)	0.0267 (14)	0.0021 (8)	-0.0032 (9)	-0.0019 (9)
N1	0.0093 (10)	0.0178 (14)	0.0147 (11)	0.0020 (9)	-0.0012 (8)	-0.0006 (10)
N2	0.0140 (11)	0.0250 (16)	0.0156 (12)	0.0012 (10)	0.0010 (10)	-0.0005 (11)
N3	0.0111 (11)	0.0222 (16)	0.0221 (14)	-0.0006 (10)	-0.0004 (10)	0.0003 (11)
N4	0.0184 (13)	0.0214 (15)	0.0167 (12)	-0.0025 (11)	-0.0054 (11)	0.0006 (11)
N5	0.0167 (13)	0.0230 (16)	0.0172 (13)	-0.0017 (11)	0.0026 (10)	-0.0014 (11)
N6	0.0188 (15)	0.049 (3)	0.030 (2)	0.0031 (17)	0.0034 (15)	0.002 (2)
N7	0.0263 (16)	0.0193 (15)	0.0158 (13)	-0.0001 (12)	-0.0030 (11)	-0.0010 (11)
O3	0.0275 (14)	0.044 (2)	0.0242 (15)	0.0026 (14)	0.0024 (12)	-0.0076 (14)
O4	0.0347 (16)	0.0330 (17)	0.0121 (11)	0.0024 (13)	-0.0015 (11)	0.0020 (11)
O5	0.0269 (14)	0.0409 (19)	0.0255 (15)	-0.0051 (13)	-0.0095 (12)	0.0083 (14)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

U1—O1	1.861 (3)	N3—H3B	0.9100
U1—O2	1.867 (3)	N3—H3C	0.9100
U1—N5	2.573 (3)	N4—H4A	0.9100
U1—N2	2.592 (3)	N4—H4B	0.9100
U1—N3	2.600 (3)	N4—H4C	0.9100
U1—N1	2.606 (3)	N5—H5A	0.9100
U1—N4	2.629 (3)	N5—H5B	0.9100
N1—H1A	0.9100	N5—H5C	0.9100
N1—H1B	0.9100	N6—H6A	0.86 (7)
N1—H1C	0.9100	N6—H6B	0.81 (8)
N2—H2A	0.9100	N6—H6C	0.63 (9)
N2—H2B	0.9100	N7—O3	1.242 (5)
N2—H2C	0.9100	N7—O5	1.253 (4)
N3—H3A	0.9100	N7—O4	1.254 (4)
O1—U1—O2	177.20 (11)	H2A—N2—H2B	109.5
O1—U1—N5	93.92 (11)	U1—N2—H2C	109.5
O2—U1—N5	86.72 (12)	H2A—N2—H2C	109.5
O1—U1—N2	92.56 (11)	H2B—N2—H2C	109.5
O2—U1—N2	88.76 (12)	U1—N3—H3A	109.5
N5—U1—N2	138.26 (11)	U1—N3—H3B	109.5
O1—U1—N3	90.52 (11)	H3A—N3—H3B	109.5
O2—U1—N3	87.34 (11)	U1—N3—H3C	109.5
N5—U1—N3	143.01 (11)	H3A—N3—H3C	109.5
N2—U1—N3	78.00 (11)	H3B—N3—H3C	109.5
O1—U1—N1	88.25 (10)	U1—N4—H4A	109.5
O2—U1—N1	94.52 (10)	U1—N4—H4B	109.5
N5—U1—N1	68.98 (10)	H4A—N4—H4B	109.5
N2—U1—N1	70.06 (10)	U1—N4—H4C	109.5

N3—U1—N1	147.94 (10)	H4A—N4—H4C	109.5
O1—U1—N4	87.96 (11)	H4B—N4—H4C	109.5
O2—U1—N4	89.59 (11)	U1—N5—H5A	109.5
N5—U1—N4	74.08 (11)	U1—N5—H5B	109.5
N2—U1—N4	147.40 (11)	H5A—N5—H5B	109.5
N3—U1—N4	69.40 (11)	U1—N5—H5C	109.5
N1—U1—N4	142.49 (10)	H5A—N5—H5C	109.5
U1—N1—H1A	109.5	H5B—N5—H5C	109.5
U1—N1—H1B	109.5	H6A—N6—H6B	104 (7)
H1A—N1—H1B	109.5	H6A—N6—H6C	103 (10)
U1—N1—H1C	109.5	H6B—N6—H6C	121 (10)
H1A—N1—H1C	109.5	O3—N7—O5	120.4 (3)
H1B—N1—H1C	109.5	O3—N7—O4	120.4 (3)
U1—N2—H2A	109.5	O5—N7—O4	119.2 (3)
U1—N2—H2B	109.5		

*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—H1A $\cdots$ O4 <sup>i</sup>	0.91	2.43	3.166 (4)	138
N1—H1A $\cdots$ O4 <sup>ii</sup>	0.91	2.47	2.996 (4)	117
N1—H1B $\cdots$ O1 <sup>iii</sup>	0.91	2.25	3.079 (4)	151
N1—H1C $\cdots$ O2 <sup>iv</sup>	0.91	2.12	3.006 (4)	165
N2—H2A $\cdots$ O4 <sup>i</sup>	0.91	2.49	3.220 (5)	138
N2—H2B $\cdots$ N6	0.91	2.14	3.024 (5)	164
N2—H2C $\cdots$ O4 <sup>ii</sup>	0.91	2.36	3.232 (5)	160
N3—H3A $\cdots$ O2 <sup>v</sup>	0.91	2.27	3.136 (5)	159
N3—H3B $\cdots$ O1 <sup>vi</sup>	0.91	2.34	3.151 (4)	149
N3—H3C $\cdots$ O5 <sup>vii</sup>	0.91	2.52	3.142 (5)	126
N4—H4A $\cdots$ O1 <sup>vi</sup>	0.91	2.37	3.219 (4)	156
N4—H4B $\cdots$ O2 <sup>v</sup>	0.91	2.26	3.086 (4)	150
N4—H4C $\cdots$ O3	0.91	2.55	3.253 (5)	134
N5—H5A $\cdots$ O5 <sup>iii</sup>	0.91	2.14	3.048 (5)	176
N5—H5B $\cdots$ O3	0.91	2.44	3.063 (5)	126
N5—H5B $\cdots$ O5	0.91	2.59	3.394 (5)	147
N5—H5C $\cdots$ O1 <sup>iii</sup>	0.91	2.37	3.273 (4)	171
N6—H6A $\cdots$ O4 <sup>vii</sup>	0.86 (7)	2.50 (7)	3.342 (6)	167 (7)
N6—H6B $\cdots$ O3 <sup>vi</sup>	0.81 (8)	2.32 (8)	3.102 (6)	162 (7)

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