

# Synthesis and crystal structure of triethylammonium hexabromidouranate(IV) dichloromethane monosolvate

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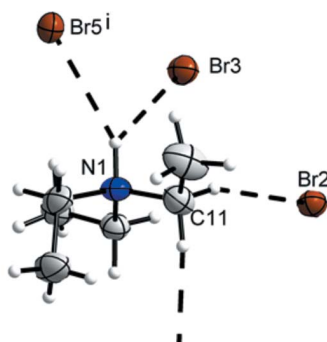
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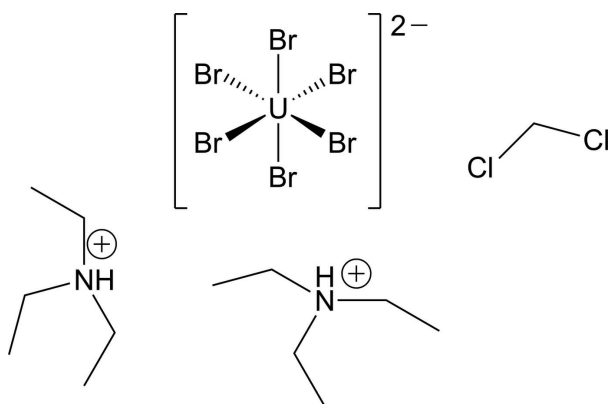
Triethylammonium hexabromidouranate(IV) dichloromethane monosolvate,  $[(C_2H_5)_3NH]_2[UBr_6] \cdot CH_2Cl_2$ , was obtained in the form of dark-brown crystals from the reaction of uranium pentabromide with  $NEt_3$  and ethylene glycol in dichloromethane at low temperature. During the progress of the reaction, the reduction of uranium(V) to uranium(IV) was observed, whose associated oxidation product could not be identified. The uranium atom of the  $[UBr_6]^{2-}$  anion is coordinated by six bromido ligands in the shape of an octahedron. Between cations, anion and solvent molecules of crystallization, numerous C—H...Hal hydrogen-bond-like interactions are present, leading to a three-dimensional network structure.

## 1. Chemical context

Starting in the 1950s, a variety of hexachloridouranates(IV) with organic cations have been investigated and described [CSD Database, Version 2.0.4, accessed 19.05.2020 (Groom *et al.*, 2016); Staritzky & Singer, 1952]. Examples of this type of compound are  $(Me_4N)_2[UCl_6]$ ,  $(Ph_4As)_2[UCl_6] \cdot CH_2Cl_2$ , or the 4,4'-bipyridin-1-ium hexachloridouranate(IV)  $(C_{10}H_{10}N_2)[UCl_6]$  (Autillo & Wilson, 2017; Müller *et al.*, 1984; Wacker *et al.*, 2019). All these compounds have a slightly distorted octahedron-shaped  $[UCl_6]^{2-}$  coordination polyhedron in common with Cl—U—Cl angles close to  $90^\circ$  and some of them, like  $[BuMeIm]_2[UCl_6]$ , feature hydrogen-bonding networks or weak hydrogen interactions (Nikitenko *et al.*, 2007). Examples of hexabromidouranates(IV) with organic cations are  $(PPh_4)_2[UBr_6] \cdot 4CH_3CN$  (Bohrer *et al.*, 1988),  $[P(C_6H_5)_3C_2H_5]_2[UBr_6]$  (Caira *et al.*, 1978) or  $(Ph_3EtP)_2[UBr_6]$  (Caira *et al.*, 1978). As in the case of the hexachloridouranates(IV), the  $[UBr_6]^{2-}$  octahedra show a slight distortion and the compounds feature an extended network of hydrogen bonds. The only two structurally elucidated examples of hexabromidouranate(V) anions,  $[UBr_6]^-$ , that show significantly shorter U—Br distances compared to  $[UBr_6]^{2-}$  anions are  $(Ph_4P)[UBr_6]$  and  $(Ph_4P)[UBr_6] \cdot 2CCl_4$  (Bohrer *et al.*, 1988). These two compounds as well as  $(PPh_4)[UBr_6] \cdot CH_2Cl_2$  serve as examples for the stability of uranium(V) in organic solvents; however, a reduction of  $U^V$  to  $U^{IV}$  was observed upon removal of the solvent (Bohrer *et al.*, 1988). During this reaction, elemental bromine was formed *via* oxidation besides the adduct  $UBr_4 \cdot CH_3CN$  (Bohrer *et al.*, 1988).

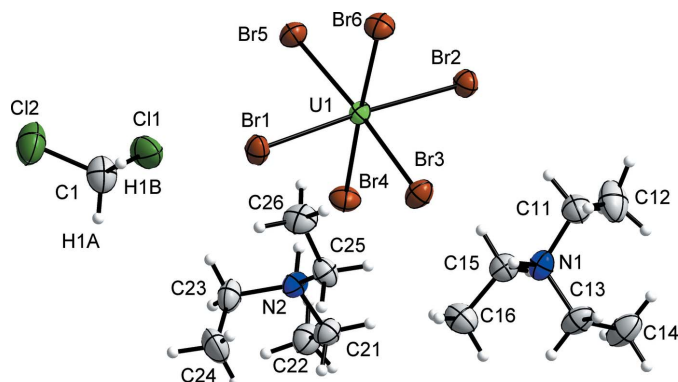


We, however, observe reduction of  $\text{UBr}_5$  to uranium(IV) as  $[\text{UBr}_6]^{2-}$  and the protonation of  $\text{N}(\text{Et}_3)$ . It is plausible that ethylene glycol serves as the proton source for the formation of the  $\text{HNEt}_3^+$  cations; however, we do not know where the glycolate anions end up. We also do not know what the reducing agent for the reduction of  $\text{U}^{\text{V}}$  to  $\text{U}^{\text{IV}}$  is, or if  $\text{UBr}_5$  is simply unstable under these conditions and is converted to  $\text{UBr}_4$  and  $0.5 \text{ Br}_2$ . We also do not know how  $\text{UBr}_5$  is dissolved, that is, whether  $\text{U}_2\text{Br}_{10}$  molecules or other mono- or polynuclear complexes, such as of glycolates, are present in solution. Elemental bromine may be present within the brown solution and act as an oxidizing agent under the formation of the  $\text{Br}^-$  anions required to constitute the  $[\text{UBr}_6]^{2-}$  anions. For the reactions to be stoichiometric, some leftover U species should have been formed that we did not observe. In summary, the detailed formation of the title compound  $(\text{Et}_3\text{NH})_2[\text{UBr}_6]\cdot\text{CH}_2\text{Cl}_2$  remains unclear.



## 2. Structural commentary

The compound triethylammonium hexabromidouranate(IV)–dichloromethane (1/1)  $(\text{Et}_3\text{NH})_2[\text{UBr}_6]\cdot\text{CH}_2\text{Cl}_2$  crystallizes in the monoclinic crystal system, space group  $P2_1/n$  (No. 14), with the lattice parameters  $a = 10.7313$  (3),  $b = 17.4534$  (4),  $c = 15.0090$  (5) Å,  $\beta = 92.0550$  (10)°,  $V = 2809.34$  (14) Å<sup>3</sup>,  $Z = 4$  at  $T = 100$  K. The uranium atom of the cation is coordinated by six bromine ligands in the shape of a slightly distorted octa-



**Figure 1**  
Section of the crystal structure of  $(\text{Et}_3\text{NH})_2[\text{UBr}_6]\cdot\text{CH}_2\text{Cl}_2$ , illustrating the asymmetric unit. Displacement ellipsoids are shown at the 70% probability level at 100 K and H atoms are drawn with an arbitrary radius.

**Table 1**  
Selected interatomic distances  $d$  (Å) for  $(\text{Et}_3\text{NH})_2[\text{UBr}_6]$ .

Atom 1	Atom 2	$d$
U1	Br1	2.7835 (4)
	Br2	2.7562 (4)
	Br3	2.7847 (5)
	Br4	2.7613 (4)
	Br5	2.7631 (5)
	Br6	2.7658 (4)
N1	C11	1.500 (6)
	C13	1.514 (6)
	C15	1.515 (5)
N2	C21	1.508 (5)
	C23	1.517 (6)
	C25	1.504 (5)
C1	C11	1.756 (5)
	C12	1.751 (5)
C11	C12	1.521 (7)
C13	C14	1.508 (6)
C15	C16	1.506 (6)
C21	C22	1.509 (6)
C23	C24	1.511 (7)
C25	C26	1.503 (6)

hedron. The atomic distances between the uranium atom and the bromido ligands range from 2.7562 (4) to 2.7847 (5) Å (Table 1). The  $\text{Br}-\text{U}-\text{Br}$  angles in the octahedron-like polyhedron range from 86.519 (13) to 94.879 (14) and show a quite significant distortion from the ideal angle of 90°. These atomic distances and angles are in good agreement with the compounds reported previously (Bohrer *et al.*, 1988; Caira *et al.*, 1978). The atomic distances of the two symmetry-independent triethylammonium cations are in good agreement with each other, as well as with the literature, for example in bis(triethylammonium) tetrachloridodioxidouranium(VI) (Gatto *et al.*, 2003; Serezhkina *et al.*, 2010; Bois *et al.*, 1976). Fig. 1 shows a section of the crystal structure.

## 3. Supramolecular features

Sections of the crystal structure, illustrating the hydrogen-bonding situation, are shown in Fig. 2. The hydrogen bonds were inspected visually and those with angles less than 134° were removed from the analysis. The Br3 and Br5 atoms of the  $[\text{UBr}_6]^{2-}$  anion act as acceptors for the bifurcated  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bond. The other  $\text{HNEt}_3^+$  cation (with N2) also forms a  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bond, however, not bifurcated. Hydrogen-bond lengths and angles are given in Table 2. Furthermore,  $\text{C}-\text{H}\cdots\text{Hal}$  hydrogen-bond-like interactions between the  $\text{HNEt}_3^+$  cations and the Br atoms of the  $[\text{UBr}_6]^{2-}$  anion as well as to the Cl atoms of the dichloromethane molecules are also present. Overall, a three-dimensional hydrogen-bonded network results. An overview of the hydrogen-bond lengths between the cations, anion and solvent molecule in the compound reported here is given in Table 2. The  $\text{C}-\text{H}\cdots\text{Br}$  hydrogen bonds in  $(\text{Ph}_3\text{EtP})_2[\text{UBr}_6]$  (Caira *et al.*, 1978) range from 2.782 (1) to 3.504 (2) Å. An example for  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bonds is  $(\text{C}_6\text{H}_8\text{NS}_3)_2[\text{UBr}_6]$  (Conradi *et al.*, 1986), with lengths of 2.81 (9) Å for the interactions. These bond lengths are comparable with the presented data.

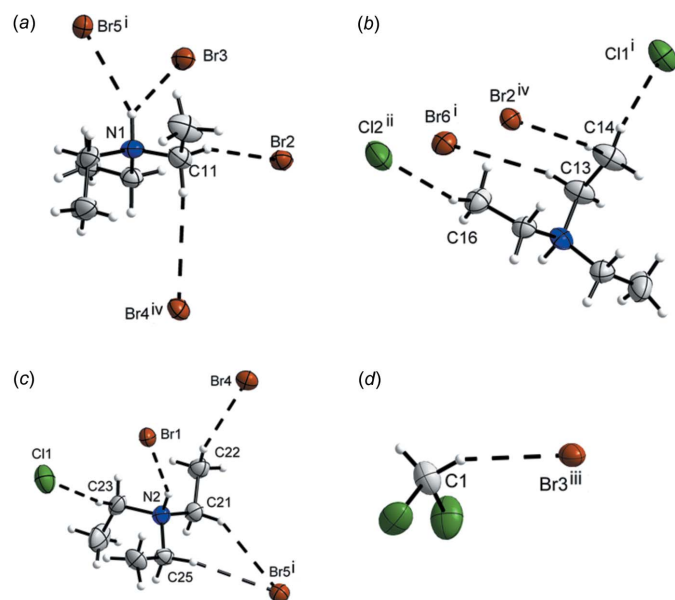
**Table 2**  
Hydrogen-bond geometry (Å, °).

<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···Br3	1.00	2.71	3.480 (3)	134
N1—H1···Br5 <sup>i</sup>	1.00	2.83	3.658 (3)	141
C11—H11A···Br2	0.99	3.13	4.070 (5)	158
C11—H11B···Br4 <sup>ii</sup>	0.99	3.24	4.184 (4)	160
C13—H13B···Br6 <sup>i</sup>	0.99	3.38	4.339 (5)	163
C14—H14A···Br2 <sup>ii</sup>	0.98	3.38	4.350 (6)	173
C14—H14B···Cl1 <sup>i</sup>	0.98	2.95	3.922 (5)	169
C16—H16B···Cl2 <sup>iii</sup>	0.98	2.97	3.904 (5)	160
N2—H2···Br1	1.00	2.59	3.499 (4)	152
C21—H21B···Br5 <sup>i</sup>	0.99	3.12	4.005 (5)	150
C22—H22C···Br4	0.98	3.20	4.139 (5)	162
C23—H23A···Cl1	0.99	2.88	3.865 (5)	171
C25—H25B···Br5 <sup>i</sup>	0.99	3.00	3.886 (4)	149
C1—H1B···Br3 <sup>iv</sup>	0.99	2.81	3.729 (5)	155

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

#### 4. Synthesis and crystallization

50 mg of UBr<sub>5</sub> (0.08 mmol, 1.00 eq) were dissolved in 2 mL of predried DCM and 0.06 mL of NEt<sub>3</sub> (40 mg, 0.39 mmol, 5.00 eq.) were added. Then, after stirring briefly, 0.01 mL of ethylene glycol (10 mg, 0.20 mmol, 2.50 eq.) were added dropwise. After two h, the reaction mixture was filtered and the obtained brown filtrate was cooled to 241 K. The product was obtained in crystalline form after three days as brown plates. A selected crystal was investigated by X-ray diffraction. As only a few crystals precipitated from the cold filtrate, the yield could not be determined, but it can be assumed that it



**Figure 2**  
The hydrogen bonds and hydrogen-bond-like interactions (dashed lines) present in the structure of the title compound. (a) and (b) show the interactions of the HNET<sup>+</sup> cation with N1, (c) of the HNET<sup>+</sup> cation with N2, and (d) shows the interactions of DCM. Displacement ellipsoids within each subfigure are shown at the 70% probability level at 100 K and H atoms are drawn with an arbitrary radius. See Table 2 for symmetry operators.

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	(C <sub>6</sub> H <sub>16</sub> N) <sub>2</sub> [UBr <sub>6</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>
<i>M<sub>r</sub></i>	1006.81
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.7318 (4), 17.4541 (4), 15.0082 (4)
$\beta$ (°)	92.055 (1)
<i>V</i> (Å <sup>3</sup> )	2809.44 (14)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	14.50
Crystal size (mm)	0.1 × 0.1 × 0.05
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Numerical ( <i>X-RED32</i> ; Stoe & Cie, 2009)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.049, 0.527
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	35494, 5945, 5307
<i>R<sub>int</sub></i>	0.065
(sin $\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.634
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.025, 0.059, 1.04
No. of reflections	5945
No. of parameters	223
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.52, -1.12

Computer programs: *X-AREA* (Stoe & Cie, 2018), *SHELXT2018/3* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *DIAMOND* (Brandenburg, 2019).

was rather low. No further analysis was carried out on the few minute crystals or the filtrate. UBr<sub>5</sub> was synthesized according to the literature (Deubner *et al.*, 2019).

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms were positioned geometrically (N—H = 1.00 Å, C—H = 0.98–0.99 Å) refined using a riding model with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N,C) or 1.5*U*<sub>eq</sub>(C<sub>methyl</sub>). The maximum and minimum residual electron densities are located close to the U atom at distances of 0.77 and 1.19 Å, respectively.

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## supporting information

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## Synthesis and crystal structure of triethylammonium hexabromidouranate(IV) dichloromethane monosolvate

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### Computing details

Data collection: *X-AREA* (Stoe & Cie, 2018); cell refinement: *X-AREA* (Stoe & Cie, 2018); data reduction: *X-AREA* (Stoe & Cie, 2018); program(s) used to solve structure: *SHELXT2018/3* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2019).

### Triethylammonium hexabromidouranate(IV) dichloromethane monosolvate

#### Crystal data



$M_r = 1006.81$

Monoclinic,  $P2_1/n$

$a = 10.7318$  (4) Å

$b = 17.4541$  (4) Å

$c = 15.0082$  (4) Å

$\beta = 92.055$  (1)°

$V = 2809.44$  (14) Å<sup>3</sup>

$Z = 4$

$F(000) = 1848$

$D_x = 2.380$  Mg m<sup>-3</sup>

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

Cell parameters from 72381 reflections

$\theta = 5.1\text{--}53.6^\circ$

$\mu = 14.50$  mm<sup>-1</sup>

$T = 100$  K

Plate, dark brown

$0.1 \times 0.1 \times 0.05$  mm

#### Data collection

STOE IPDS 2T

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus

Planar graphite monochromator

Detector resolution: 6.67 pixels mm<sup>-1</sup>

rotation method,  $\omega$  scans

Absorption correction: numerical (X-Red32; Stoe & Cie, 2009)

$T_{\min} = 0.049$ ,  $T_{\max} = 0.527$

35494 measured reflections

5945 independent reflections

5307 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.065$

$\theta_{\max} = 26.8^\circ$ ,  $\theta_{\min} = 2.6^\circ$

$h = -13 \rightarrow 13$

$k = -22 \rightarrow 22$

$l = -19 \rightarrow 18$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.059$

$S = 1.04$

5945 reflections

223 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 6.7371P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 1.52$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.12$  e Å<sup>-3</sup>

*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	0.70763 (2)	0.60417 (2)	0.25294 (2)	0.01693 (5)
Br1	0.69695 (4)	0.57164 (3)	0.43407 (3)	0.02583 (10)
Br2	0.71934 (4)	0.62538 (3)	0.07145 (3)	0.02426 (10)
Br3	0.79682 (4)	0.45554 (3)	0.23313 (3)	0.02729 (10)
Br4	0.46676 (4)	0.55130 (3)	0.22569 (3)	0.02739 (10)
Br5	0.61892 (4)	0.74956 (2)	0.28651 (3)	0.02490 (10)
Br6	0.95008 (4)	0.65689 (3)	0.27283 (3)	0.02697 (10)
C11	0.80839 (13)	0.55597 (8)	0.65867 (8)	0.0411 (3)
C12	0.83159 (13)	0.58050 (10)	0.85069 (9)	0.0513 (4)
N1	0.7139 (3)	0.3577 (2)	0.0379 (2)	0.0233 (8)
H1	0.755481	0.354489	0.098517	0.028*
N2	0.7104 (3)	0.3716 (2)	0.4459 (2)	0.0232 (8)
H2	0.705708	0.424063	0.419282	0.028*
C1	0.8582 (4)	0.5179 (3)	0.7622 (3)	0.0350 (11)
H1A	0.813690	0.469171	0.772342	0.042*
H1B	0.948470	0.506395	0.761006	0.042*
C11	0.7928 (4)	0.4099 (3)	-0.0159 (3)	0.0305 (10)
H11A	0.798906	0.460352	0.014011	0.037*
H11B	0.751630	0.417679	-0.075281	0.037*
C12	0.9236 (4)	0.3788 (4)	-0.0280 (4)	0.0439 (14)
H12A	0.960175	0.363457	0.030062	0.066*
H12B	0.975348	0.418558	-0.054084	0.066*
H12C	0.919360	0.334222	-0.067749	0.066*
C13	0.7052 (5)	0.2763 (3)	0.0032 (3)	0.0306 (10)
H13A	0.789983	0.253987	0.003254	0.037*
H13B	0.655161	0.245525	0.044208	0.037*
C14	0.6472 (5)	0.2707 (3)	-0.0896 (3)	0.0387 (12)
H14A	0.561944	0.290737	-0.089751	0.058*
H14B	0.645537	0.216946	-0.108520	0.058*
H14C	0.696590	0.300684	-0.130777	0.058*
C15	0.5882 (4)	0.3948 (3)	0.0504 (3)	0.0244 (9)
H15A	0.601033	0.447669	0.072758	0.029*
H15B	0.542776	0.397995	-0.008087	0.029*
C16	0.5098 (4)	0.3514 (3)	0.1146 (3)	0.0322 (11)
H16A	0.484504	0.302216	0.087991	0.048*
H16B	0.435415	0.381437	0.127367	0.048*
H16C	0.558378	0.342157	0.170045	0.048*
C21	0.6301 (4)	0.3208 (3)	0.3864 (3)	0.0260 (9)
H21A	0.626464	0.269114	0.413275	0.031*



H21B	0.669358	0.315813	0.327985	0.031*
C22	0.4989 (4)	0.3505 (3)	0.3715 (3)	0.0310 (10)
H22A	0.455318	0.348800	0.427708	0.046*
H22B	0.454521	0.318541	0.327033	0.046*
H22C	0.501713	0.403488	0.349993	0.046*
C23	0.6641 (4)	0.3789 (3)	0.5399 (3)	0.0296 (10)
H23A	0.709967	0.420914	0.570805	0.036*
H23B	0.574683	0.392884	0.536600	0.036*
C24	0.6800 (6)	0.3064 (3)	0.5941 (3)	0.0445 (13)
H24A	0.636358	0.264126	0.563271	0.067*
H24B	0.644987	0.313862	0.652859	0.067*
H24C	0.768859	0.294031	0.601240	0.067*
C25	0.8449 (4)	0.3475 (3)	0.4436 (3)	0.0248 (9)
H25A	0.854298	0.296273	0.471340	0.030*
H25B	0.868916	0.343198	0.380740	0.030*
C26	0.9315 (4)	0.4027 (3)	0.4915 (3)	0.0325 (11)
H26A	0.918147	0.454356	0.467310	0.049*
H26B	1.018010	0.387174	0.483028	0.049*
H26C	0.914733	0.402615	0.555219	0.049*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
U1	0.01705 (8)	0.01736 (9)	0.01627 (7)	0.00032 (6)	-0.00099 (5)	-0.00022 (5)
Br1	0.0311 (2)	0.0274 (2)	0.01893 (18)	0.00404 (18)	0.00139 (16)	0.00121 (17)
Br2	0.0261 (2)	0.0274 (2)	0.01914 (18)	-0.00121 (17)	-0.00094 (16)	-0.00011 (16)
Br3	0.0308 (2)	0.0229 (2)	0.0278 (2)	0.00371 (17)	-0.00318 (17)	-0.00230 (17)
Br4	0.02038 (19)	0.0287 (2)	0.0329 (2)	-0.00374 (17)	-0.00104 (17)	0.00114 (18)
Br5	0.0270 (2)	0.0205 (2)	0.0272 (2)	0.00144 (17)	0.00110 (16)	-0.00114 (17)
Br6	0.02052 (19)	0.0305 (2)	0.0297 (2)	-0.00311 (17)	-0.00316 (16)	-0.00108 (18)
Cl1	0.0534 (7)	0.0411 (7)	0.0285 (6)	-0.0082 (6)	-0.0010 (5)	0.0058 (5)
Cl2	0.0456 (7)	0.0706 (10)	0.0377 (7)	-0.0045 (7)	0.0036 (6)	-0.0211 (7)
N1	0.0237 (17)	0.026 (2)	0.0199 (17)	0.0037 (15)	-0.0050 (14)	-0.0013 (15)
N2	0.0231 (17)	0.0223 (19)	0.0242 (18)	-0.0015 (15)	-0.0009 (14)	-0.0026 (15)
C1	0.027 (2)	0.047 (3)	0.031 (2)	0.004 (2)	-0.0007 (19)	-0.003 (2)
C11	0.027 (2)	0.036 (3)	0.028 (2)	-0.005 (2)	-0.0007 (18)	-0.002 (2)
C12	0.027 (2)	0.069 (4)	0.036 (3)	-0.001 (3)	0.006 (2)	-0.007 (3)
C13	0.038 (2)	0.020 (2)	0.033 (2)	0.0048 (19)	-0.008 (2)	0.0000 (19)
C14	0.053 (3)	0.029 (3)	0.033 (2)	0.004 (2)	-0.013 (2)	-0.005 (2)
C15	0.021 (2)	0.025 (2)	0.027 (2)	0.0018 (17)	-0.0027 (17)	-0.0005 (18)
C16	0.026 (2)	0.040 (3)	0.031 (2)	-0.003 (2)	-0.0024 (18)	0.005 (2)
C21	0.024 (2)	0.027 (2)	0.028 (2)	-0.0003 (18)	-0.0003 (17)	-0.0036 (18)
C22	0.024 (2)	0.035 (3)	0.034 (2)	0.001 (2)	0.0015 (18)	-0.006 (2)
C23	0.025 (2)	0.037 (3)	0.027 (2)	0.003 (2)	0.0051 (18)	-0.009 (2)
C24	0.058 (3)	0.045 (3)	0.032 (3)	-0.001 (3)	0.021 (2)	0.006 (2)
C25	0.0187 (19)	0.030 (3)	0.026 (2)	0.0036 (18)	0.0041 (16)	0.0029 (18)
C26	0.024 (2)	0.038 (3)	0.035 (2)	-0.004 (2)	-0.0069 (19)	0.000 (2)

*Geometric parameters (Å, °)*

U1—Br2	2.7562 (4)	C14—H14A	0.9800
U1—Br4	2.7613 (4)	C14—H14B	0.9800
U1—Br5	2.7631 (5)	C14—H14C	0.9800
U1—Br6	2.7658 (4)	C15—C16	1.506 (6)
U1—Br1	2.7835 (4)	C15—H15A	0.9900
U1—Br3	2.7847 (5)	C15—H15B	0.9900
C11—C1	1.756 (5)	C16—H16A	0.9800
C12—C1	1.751 (5)	C16—H16B	0.9800
N1—C11	1.500 (6)	C16—H16C	0.9800
N1—C13	1.514 (6)	C21—C22	1.509 (6)
N1—C15	1.515 (5)	C21—H21A	0.9900
N1—H1	1.0000	C21—H21B	0.9900
N2—C25	1.504 (5)	C22—H22A	0.9800
N2—C21	1.508 (5)	C22—H22B	0.9800
N2—C23	1.517 (6)	C22—H22C	0.9800
N2—H2	1.0000	C23—C24	1.511 (7)
C1—H1A	0.9900	C23—H23A	0.9900
C1—H1B	0.9900	C23—H23B	0.9900
C11—C12	1.521 (7)	C24—H24A	0.9800
C11—H11A	0.9900	C24—H24B	0.9800
C11—H11B	0.9900	C24—H24C	0.9800
C12—H12A	0.9800	C25—C26	1.503 (6)
C12—H12B	0.9800	C25—H25A	0.9900
C12—H12C	0.9800	C25—H25B	0.9900
C13—C14	1.508 (6)	C26—H26A	0.9800
C13—H13A	0.9900	C26—H26B	0.9800
C13—H13B	0.9900	C26—H26C	0.9800
Br2—U1—Br4	88.519 (13)	H14A—C14—H14B	109.5
Br2—U1—Br5	94.879 (14)	C13—C14—H14C	109.5
Br4—U1—Br5	90.407 (14)	H14A—C14—H14C	109.5
Br2—U1—Br6	89.194 (13)	H14B—C14—H14C	109.5
Br4—U1—Br6	177.674 (14)	C16—C15—N1	112.6 (4)
Br5—U1—Br6	90.214 (14)	C16—C15—H15A	109.1
Br2—U1—Br1	175.943 (14)	N1—C15—H15A	109.1
Br4—U1—Br1	90.307 (14)	C16—C15—H15B	109.1
Br5—U1—Br1	89.011 (13)	N1—C15—H15B	109.1
Br6—U1—Br1	91.945 (13)	H15A—C15—H15B	107.8
Br2—U1—Br3	89.519 (13)	C15—C16—H16A	109.5
Br4—U1—Br3	89.792 (14)	C15—C16—H16B	109.5
Br5—U1—Br3	175.601 (13)	H16A—C16—H16B	109.5
Br6—U1—Br3	89.760 (14)	C15—C16—H16C	109.5
Br1—U1—Br3	86.593 (13)	H16A—C16—H16C	109.5
C11—N1—C13	114.4 (4)	H16B—C16—H16C	109.5
C11—N1—C15	109.2 (3)	N2—C21—C22	113.4 (4)
C13—N1—C15	113.5 (3)	N2—C21—H21A	108.9



C11—N1—H1	106.3	C22—C21—H21A	108.9
C13—N1—H1	106.3	N2—C21—H21B	108.9
C15—N1—H1	106.3	C22—C21—H21B	108.9
C25—N2—C21	110.5 (3)	H21A—C21—H21B	107.7
C25—N2—C23	113.0 (3)	C21—C22—H22A	109.5
C21—N2—C23	113.6 (3)	C21—C22—H22B	109.5
C25—N2—H2	106.3	H22A—C22—H22B	109.5
C21—N2—H2	106.3	C21—C22—H22C	109.5
C23—N2—H2	106.3	H22A—C22—H22C	109.5
C12—C1—C11	112.5 (3)	H22B—C22—H22C	109.5
C12—C1—H1A	109.1	C24—C23—N2	113.3 (4)
C11—C1—H1A	109.1	C24—C23—H23A	108.9
C12—C1—H1B	109.1	N2—C23—H23A	108.9
C11—C1—H1B	109.1	C24—C23—H23B	108.9
H1A—C1—H1B	107.8	N2—C23—H23B	108.9
N1—C11—C12	112.8 (4)	H23A—C23—H23B	107.7
N1—C11—H11A	109.0	C23—C24—H24A	109.5
C12—C11—H11A	109.0	C23—C24—H24B	109.5
N1—C11—H11B	109.0	H24A—C24—H24B	109.5
C12—C11—H11B	109.0	C23—C24—H24C	109.5
H11A—C11—H11B	107.8	H24A—C24—H24C	109.5
C11—C12—H12A	109.5	H24B—C24—H24C	109.5
C11—C12—H12B	109.5	C26—C25—N2	112.8 (4)
H12A—C12—H12B	109.5	C26—C25—H25A	109.0
C11—C12—H12C	109.5	N2—C25—H25A	109.0
H12A—C12—H12C	109.5	C26—C25—H25B	109.0
H12B—C12—H12C	109.5	N2—C25—H25B	109.0
C14—C13—N1	113.4 (4)	H25A—C25—H25B	107.8
C14—C13—H13A	108.9	C25—C26—H26A	109.5
N1—C13—H13A	108.9	C25—C26—H26B	109.5
C14—C13—H13B	108.9	H26A—C26—H26B	109.5
N1—C13—H13B	108.9	C25—C26—H26C	109.5
H13A—C13—H13B	107.7	H26A—C26—H26C	109.5
C13—C14—H14A	109.5	H26B—C26—H26C	109.5
C13—C14—H14B	109.5		
C13—N1—C11—C12	-54.2 (5)	C25—N2—C21—C22	-168.9 (4)
C15—N1—C11—C12	177.2 (4)	C23—N2—C21—C22	62.8 (5)
C11—N1—C13—C14	-61.4 (5)	C25—N2—C23—C24	-56.5 (5)
C15—N1—C13—C14	64.9 (5)	C21—N2—C23—C24	70.5 (5)
C11—N1—C15—C16	-171.9 (4)	C21—N2—C25—C26	171.9 (4)
C13—N1—C15—C16	59.1 (5)	C23—N2—C25—C26	-59.4 (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—H1 $\cdots$ Br3	1.00	2.71	3.480 (3)	134
N1—H1 $\cdots$ Br5 <sup>i</sup>	1.00	2.83	3.658 (3)	141

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C11—H11A···Br2	0.99	3.13	4.070 (5)	158
C11—H11B···Br4 <sup>ii</sup>	0.99	3.24	4.184 (4)	160
C13—H13B···Br6 <sup>i</sup>	0.99	3.38	4.339 (5)	163
C14—H14A···Br2 <sup>ii</sup>	0.98	3.38	4.350 (6)	173
C14—H14B···C11 <sup>i</sup>	0.98	2.95	3.922 (5)	169
C16—H16B···C12 <sup>iii</sup>	0.98	2.97	3.904 (5)	160
N2—H2···Br1	1.00	2.59	3.499 (4)	152
C21—H21B···Br5 <sup>i</sup>	0.99	3.12	4.005 (5)	150
C22—H22C···Br4	0.98	3.20	4.139 (5)	162
C23—H23A···C11	0.99	2.88	3.865 (5)	171
C25—H25B···Br5 <sup>i</sup>	0.99	3.00	3.886 (4)	149
C1—H1B···Br3 <sup>iv</sup>	0.99	2.81	3.729 (5)	155

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