



$(\text{NH}_4)_2[\text{UO}_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}$, a new uranyl tetrachloride with ammonium charge-balancing cations

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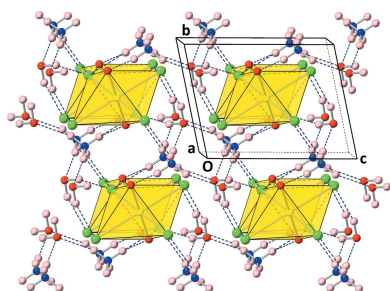
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A new uranyl tetrachloride salt with chemical formula, $(\text{NH}_4)_2[\text{UO}_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}$, namely, diammonium uranyl tetrachloride dihydrate, **1**, was prepared and crystallized *via* slow evaporation from a solution of 2 M hydrochloric acid. As confirmed by powder X-ray diffraction, the title compound crystallizes with an ammonium chloride impurity that formed as a result of the breakdown of a triazine precursor. The $(\text{UO}_2\text{Cl}_4)^{2-}$ dianion is charge balanced by ammonium cations, while an extensive hydrogen-bond network donated from structural water molecules stabilize the overall assembly. Compound **1** adds to the extensive collection of actinyl tetrachloride salts, but it represents the first without an alkali cation for purely inorganic compounds. Diffuse reflectance and luminescence spectra show typical absorption and emission behavior, respectively, of uranyl materials.

1. Chemical context

Hexavalent actinides such as uranium, neptunium, and plutonium exist in aqueous solution as the linear triatomic actinyl cation, with formula $(\text{AnO}_2)^{2+}$. The actinyl ion coordinates a variety of poly- and mono-atomic anions such that four to six atoms bond in the equatorial plane (Burns, 2005; Lussier *et al.*, 2016). In part due to their ease of synthesis, structural simplicity, and high symmetry, the actinyl tetrahalide family of compounds has remained a relevant subclass of materials over several decades and has led to a deeper understanding of actinide electronic structure, bonding, and optical properties, among many others. The actinyl tetrahalides have general formula $(\text{AnO}_2\text{X}_4)^{2-}$ (where $\text{An} = \text{U}^{\text{VI}}$, Np^{VI} , and Pu^{VI} and $\text{X} = \text{Cl}^-$ and Br^-) and have been studied to investigate periodic trends in *f*-element chemistry. Of the numerous compounds that include this anionic complex, the Cs^+ salt with formula $\text{Cs}_2(\text{AnO}_2\text{Cl}_4)$ has been one of the most extensively characterized actinyl compounds. The uranyl structure was first reported in 1966 (Hall *et al.*, 1966) with an improved model reported in 1991 (Watkin *et al.*, 1991). In that time, it was used to quantitatively assign infrared (Ohwada, 1975) and Raman (Ohwada, 1980) active bands of the uranyl ion, which were found to be at 916 cm^{-1} and 831 cm^{-1} , respectively. Improvements in analytical (*i.e.* X-ray absorption spectroscopies) and computational techniques (*i.e.* density functional theory calculations) over time have advanced our understanding in the electronic and molecular orbital energies of the uranyl ion in $\text{Cs}_2(\text{UO}_2\text{Cl}_4)$, providing strong evidence that actinide atoms can bind with significant covalent character (Denning, 2007; Vitova *et al.*, 2015). Luminescence



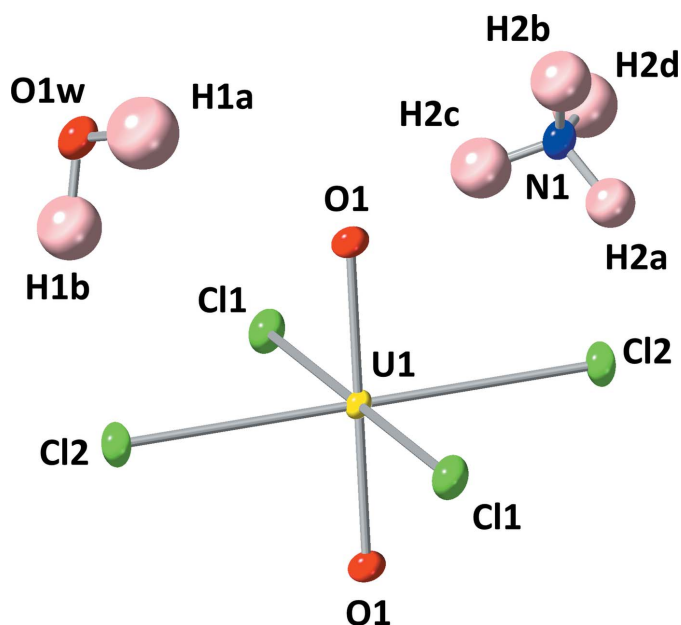


Figure 1
The uranyl tetrachloride anionic unit along with a crystallographically unique water molecule and ammonium cation. Displacement ellipsoids for non-hydrogen atoms are shown at 50% probability.

spectroscopy, Raman spectroscopy, and computational works have also been used to study bond-length changes of the uranyl ion with respect to different pressures in $\text{Cs}_2(\text{UO}_2\text{Cl}_4)$ (Osman *et al.*, 2016; Warzecha *et al.*, 2019). Beyond the Cs salt, systematic studies into actinyl bond strength changes as a function of metal center (*i.e.* $\text{An} = \text{U}^{\text{VI}}$, Np^{VI} and Pu^{VI}) have been reported for organic-based counter-cations (Schnaars & Wilson, 2013; Surbella III *et al.*, 2017; Schnaars & Wilson, 2018). Quite recently, focus has been placed on the cationic influence on supramolecular assembly as well as actinyl bond-strength changes (Schnaars & Wilson, 2013; Surbella III *et al.*, 2016; Carter *et al.*, 2018; Pyrch *et al.*, 2020; Augustine *et al.*,

2023). Despite these numerous studies with actinyl tetrahalide species, we report a new inorganic uranyl tetrachloride not charge-balanced by an alkali cation, with formula $(\text{NH}_4)_2(\text{UO}_2\text{Cl}_4) \cdot 2\text{H}_2\text{O}$ (compound **1**).

2. Structural commentary

Compound **1** crystallizes in the space group $P\bar{1}$. The uranyl tetrachloride dianion $(\text{UO}_2\text{Cl}_4)^{2-}$ is composed of a U^{VI} metal center that is coordinated to two terminal, axial oxygen atoms and four equatorial chlorine atoms as shown in Fig. 1. The $(\text{UO}_2\text{Cl}_4)^{2-}$ dianion adopts a square-bipyramidal coordination geometry with D_{4h} point group symmetry. The U^{VI} atom sits on a center of inversion symmetry, resulting in a linear uranyl $(\text{UO}_2)^{2+}$ cation with a $\text{U1}-\text{O1}$ bond distance of 1.7745 (14) Å and $\text{O1}-\text{U1}-\text{O1}$ angle of 180°. The U^{VI} atom is also coordinated to two crystallographically unique chlorine atoms with $\text{U1}-\text{Cl1}$ and $\text{U1}-\text{Cl2}$ bond distances of 2.6752 (5) Å and 2.6623 (4) Å, respectively. The two $\text{Cl1}-\text{U1}-\text{Cl2}$ bond angles measure 88.855 (15)° and 91.145 (15)°, and $\text{O1}-\text{U1}-\text{Cl1}$, bond angles also slightly deviate from 90°. The $\text{U}-\text{O}$ (Lussier *et al.*, 2016) and $\text{U}-\text{Cl}$ (Surbella III *et al.*, 2016) bond lengths are typical for these compounds. The structure contains one crystallographically unique structural water molecule (O1w) with two $\text{O}-\text{H}$ covalent bonds with restrained bond lengths near 0.95 Å, and one crystallographically unique ammonium cation (N1) is present to provide charge balance to the overall structure. There are four $\text{N}-\text{H}$ covalent bonds with restrained bond lengths that are approximately 0.87 Å. The extended crystal structure is shown in Fig. 2.

3. Supramolecular features

A hydrogen-bond network consisting of seven unique interactions exists between ammonium cations, water molecules, and uranyl tetrachloride units as depicted in Fig. 3 and as

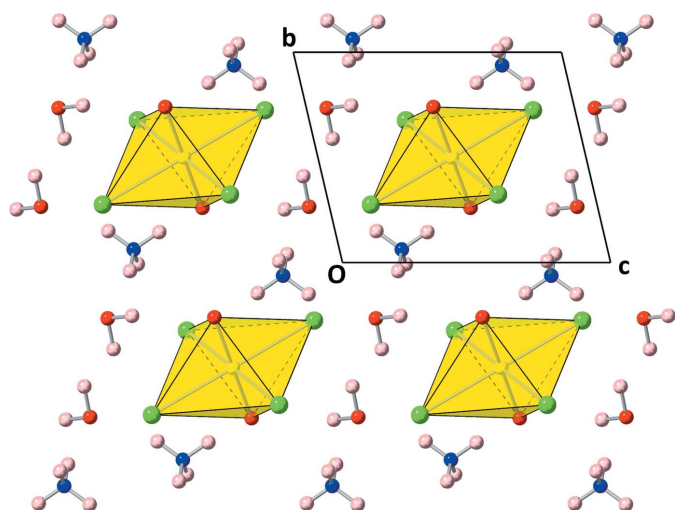


Figure 2
The crystal packing observed in compound **1** as viewed along the a -axis.

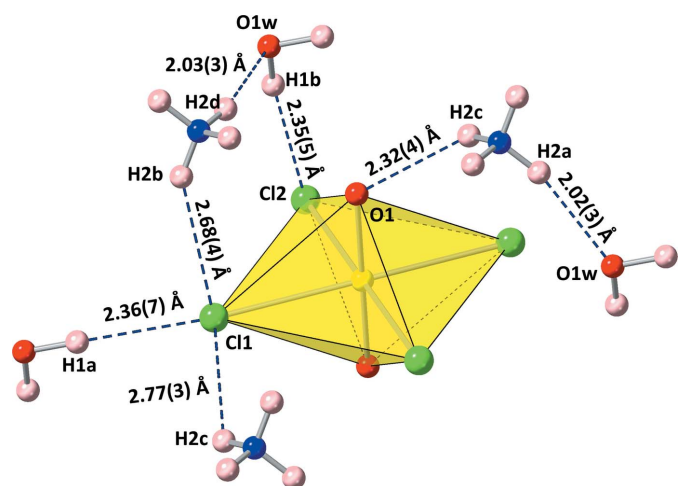


Figure 3
The seven unique hydrogen-bond interactions shown with the hydrogen-bond distances from donor hydrogen atom to acceptor atom.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1w-H1A\cdots Cl1^i$	0.95 (6)	2.36 (7)	3.283 (2)	165 (7)
$O1w-H1B\cdots Cl2^{ii}$	0.95 (5)	2.35 (5)	3.268 (2)	163 (5)
$N1-H2A\cdots O1w$	0.87 (3)	2.02 (3)	2.843 (2)	157 (3)
$N1-H2B\cdots Cl1^{iii}$	0.87 (4)	2.68 (4)	3.441 (2)	148 (3)
$N1-H2C\cdots O1$	0.87 (2)	2.32 (4)	3.014 (3)	137 (4)
$N1-H2C\cdots Cl1^{iv}$	0.87 (2)	2.77 (3)	3.4060 (17)	131 (4)
$N1-H2D\cdots O1w^v$	0.87 (3)	2.03 (3)	2.887 (3)	169 (3)

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

tabulated in Table 1. Each water molecule donates two hydrogen bonds *via* H1A and H1B donor atoms to two separate uranyl tetrachloride complexes. On the other hand, each ammonium cation donates hydrogen bonds in three dimensions to three separate uranyl tetrachloride units and two separate water molecules, stabilizing the overall crystal structure into a complex network. Fig. 4 shows the hydrogen-bond network in the extended structure.

4. Database survey

Compound **1** is the first inorganic uranyl tetrachloride charge-balanced with a non-alkali metal in the Inorganic Crystal Structure Database (Zagorac *et al.*, 2019). With respect to structures in the ICSD, Cs salts of the $(AnO_2Cl_4)^{2-}$ species have been reported for U (Hall *et al.*, 1966; Watkin *et al.*, 1991; Tutov *et al.*, 1991; Schnaars & Wilson, 2013), Np (Wilkerson *et al.*, 2007), and Pu (Wilkerson & Scott, 2008; Schnaars & Wilson, 2013). Other charge-balancing cations reported in the ICSD for U^{VI} and Pu^{VI} include Rb (Anson *et al.*, 1996; Schnaars & Wilson, 2013) and tetramethylammonium (Schnaars & Wilson, 2013), while that of Np includes $(UO_2Cl_4)^{2-}$ -doped Np^{VI} (Wilkerson & Berg, 2009) and a

mixed $Np^{V/VI}$ oxidation state Cs salt (Alcock *et al.*, 1986). Although there is a tetramethylammonium salt in the ICSD, we consider it as a better member of the Crystal Structure Database (CSD) given the presence of organic-based (*i.e.* C–H bonds) components in the structure (Groom *et al.*, 2016).

With respect to the CSD, there are numerous reports with ammonium-based charge-balancing species (Di Sipio *et al.*, 1974*a,b*; Bois *et al.*, 1976*a,b*; Rogers *et al.*, 1987; Gatto *et al.*, 2004; Schnaars & Wilson, 2013; Biswas *et al.*, 2017; Serezkhina *et al.*, 2021). Compound **1** has ammonium with a water molecule, while one report has ammonium with crown ethers (Rogers *et al.*, 1987). The other ammonium-based cations include organic-functional groups (Di Sipio *et al.*, 1974*a,b*; Bois *et al.*, 1976*a,b*; Gatto *et al.*, 2004; Schnaars & Wilson, 2013; Biswas *et al.*, 2017; Serezkhina *et al.*, 2021). Other types of cations that charge-balance $(UO_2Cl_4)^{2-}$ in the CSD include pyridinium-based (Graziani *et al.*, 1975; Bombieri *et al.*, 1978; Marsh, 1988; Pospieszna *et al.*, 2008; Deifel & Cahill, 2009; Baker *et al.*, 2010; Andrews & Cahill, 2012; Lhoste *et al.*, 2013; Hashem *et al.*, 2013; Surbella III *et al.*, 2016, 2017; Carter *et al.*, 2018; Mishra *et al.*, 2019; Pyrch *et al.*, 2020), phenanthroline-based (Di Sipio *et al.*, 1981), imidazolium-based (Zalkin *et al.*, 1983; Qu *et al.*, 2014; Kohlgruber, 2022), and phosphonium-based (Brown *et al.*, 1996; Schnaars & Wilson, 2014) species. Other $(UO_2Cl_4)^{2-}$ complexes have crystallized in the presence of separate metal complexes (Moody & Ryan, 1979; Rogers *et al.*, 1987, 1990; Pons y Moll *et al.*, 2001; Hashem *et al.*, 2014; Falaise *et al.*, 2015; Zhang *et al.*, 2017; Schöne *et al.*, 2018), crown ethers (Wang *et al.*, 1986; Rogers *et al.*, 1987, 1991; Rogers & Benning, 1991; Evans *et al.*, 2002) and porphyrins (Mishra *et al.*, 2019). In total, there are over 60 known uranyl tetrachloride crystal structures in the CSD. Reference codes for these compounds can be found in the supporting information.

5. Synthesis and crystallization

Concentrated hydrochloric acid, HCl, (Sigma-Aldrich, 37%) was diluted to 2 M. Then, 0.0366 g (0.44 mmol) of 1,3,5-triazine (Sigma-Aldrich, 97.0%) was dissolved into 1 mL of 2 M HCl in a 1-dram borosilicate glass reaction vial. Uranyl acetate dihydrate (0.10216 g; 2.4 mmol) was added to this solution and allowed to dissolve completely. The vial was placed uncapped in a 20 mL centrifuge tube on a bed of desiccant. The centrifuge tube was capped, and the reaction solution was allowed to evaporate for 3 weeks until large yellow crystals formed. It was noticed that compound **1** partially dissolves in ethanol, affecting the preparation for characterization beyond single-crystal X-ray diffraction. Powder-diffraction data was collected using a Rigaku Ultima IV Diffractometer with $Cu K\alpha$ radiation and a linear position-sensitive detector. The analysis revealed an ammonium chloride, NH_4Cl , impurity phase along with compound **1**. Diffuse reflectance and luminescence spectra were also collected for the mixed-phase material and can be found in the supporting information along with the powder-diffraction data.

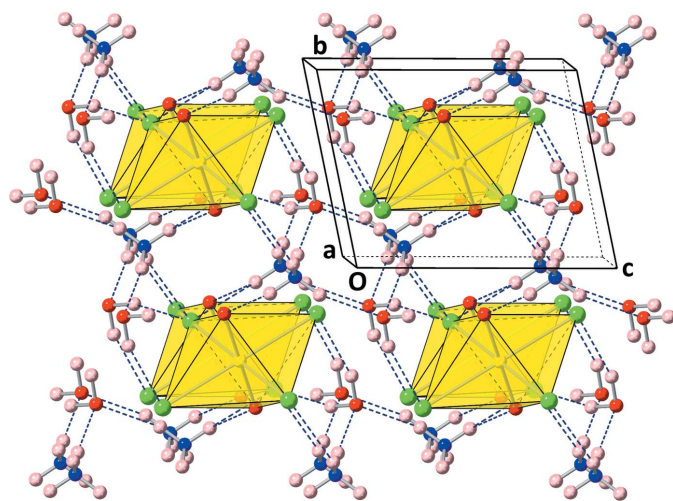


Figure 4
The crystal packing along with the hydrogen-bond network observed in compound **1** as viewed slightly offset along the *a*-axis.

Table 2

Experimental details.

Crystal data	
Chemical formula	(NH ₄) ₂ [UO ₂ Cl ₄]·2H ₂ O
<i>M</i> _r	483.95
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.6574 (4), 6.6954 (4), 7.4018 (4)
α , β , γ (°)	99.827 (2), 93.879 (2), 117.354 (1)
<i>V</i> (Å ³)	284.69 (3)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	15.17
Crystal size (mm)	0.10 × 0.03 × 0.03
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.460, 0.747
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	24049, 2803, 2803
<i>R</i> _{int}	0.042
(sin θ/λ) _{max} (Å ⁻¹)	0.842
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.017, 0.041, 1.09
No. of reflections	2803
No. of parameters	76
No. of restraints	12
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	2.94, -1.97

Computer programs: *APEX4* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *CrystalMaker* (CrystalMaker, 2014), and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in Fourier difference maps, and their positions refined with positional restraints.

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supporting information

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(NH₄)₂[UO₂Cl₄]·2H₂O, a new uranyl tetrachloride with ammonium charge-balancing cations

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Computing details

Data collection: *APEX4* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *CrystalMaker* (*CrystalMaker*, 2014); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

Diammonium uranyl tetrachloride dihydrate

Crystal data

(NH₄)₂[UO₂Cl₄]·2H₂O

M_r = 483.95

Triclinic, *P*1

a = 6.6574 (4) Å

b = 6.6954 (4) Å

c = 7.4018 (4) Å

α = 99.827 (2)°

β = 93.879 (2)°

γ = 117.354 (1)°

V = 284.69 (3) Å³

Z = 1

F(000) = 218

D_x = 2.823 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 9764 reflections

θ = 3.5–36.7°

μ = 15.17 mm⁻¹

T = 100 K

Block, yellow

0.10 × 0.03 × 0.03 mm

Data collection

Bruker D8 Venture
diffractometer

Radiation source: microsource Diamond II

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

T_{min} = 0.460, *T_{max}* = 0.747

24049 measured reflections

2803 independent reflections

2803 reflections with *I* > 2σ(*I*)

R_{int} = 0.042

θ_{max} = 36.8°, θ_{min} = 3.5°

h = -11→11

k = -11→11

l = -12→12

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.017

wR(*F*²) = 0.041

S = 1.09

2803 reflections

76 parameters

12 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

w = 1/[σ²(*F_o*²) + (0.0306*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 2.94 e Å⁻³

Δρ_{min} = -1.97 e Å⁻³

Special details

Geometry. All estimated standard deviations (esds), except those pertaining to the dihedral angle between two least squares (ls) planes, are estimated using the full covariance matrix.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
U1	0.500000	0.500000	0.500000	0.00924 (3)
Cl1	0.11039 (7)	0.32334 (9)	0.63968 (6)	0.01683 (7)
Cl2	0.27372 (8)	0.27569 (9)	0.15652 (6)	0.01779 (7)
O1	0.4614 (3)	0.7395 (3)	0.4746 (2)	0.0157 (2)
O1W	0.2602 (3)	0.7346 (3)	1.0758 (2)	0.0193 (2)
H1A	0.173 (10)	0.747 (13)	1.169 (7)	0.060 (19)*
H1B	0.253 (11)	0.589 (5)	1.071 (9)	0.048 (16)*
N1	0.2678 (3)	0.9378 (3)	0.7673 (2)	0.0165 (2)
H2A	0.227 (6)	0.850 (5)	0.846 (4)	0.028 (11)*
H2B	0.186 (5)	1.008 (6)	0.765 (5)	0.042 (14)*
H2C	0.247 (7)	0.855 (6)	0.657 (2)	0.042 (14)*
H2D	0.412 (2)	1.040 (5)	0.800 (5)	0.049 (16)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.01069 (4)	0.01103 (4)	0.00762 (4)	0.00584 (3)	0.00291 (2)	0.00367 (2)
Cl1	0.01357 (14)	0.02264 (19)	0.01467 (15)	0.00771 (14)	0.00622 (12)	0.00655 (14)
Cl2	0.01902 (16)	0.02084 (18)	0.01029 (14)	0.00814 (14)	0.00083 (12)	0.00047 (13)
O1	0.0210 (5)	0.0150 (5)	0.0159 (5)	0.0113 (5)	0.0057 (4)	0.0067 (4)
O1W	0.0189 (6)	0.0234 (7)	0.0175 (6)	0.0096 (5)	0.0063 (5)	0.0093 (5)
N1	0.0180 (6)	0.0189 (6)	0.0126 (5)	0.0085 (5)	0.0027 (5)	0.0045 (5)

Geometric parameters (\AA , $^\circ$)

U1—O1	1.7745 (14)	O1W—H1A	0.948 (10)
U1—O1 ⁱ	1.7745 (14)	O1W—H1B	0.947 (10)
U1—Cl2	2.6623 (4)	N1—H2A	0.868 (9)
U1—Cl2 ⁱ	2.6623 (4)	N1—H2B	0.872 (9)
U1—Cl1	2.6752 (5)	N1—H2C	0.870 (9)
U1—Cl1 ⁱ	2.6752 (5)	N1—H2D	0.871 (9)
O1—U1—O1 ⁱ	180.0	O1 ⁱ —U1—Cl1 ⁱ	89.87 (5)
O1—U1—Cl2	90.32 (5)	Cl2—U1—Cl1 ⁱ	88.855 (15)
O1 ⁱ —U1—Cl2	89.68 (5)	Cl2 ⁱ —U1—Cl1 ⁱ	91.145 (15)
O1—U1—Cl2 ⁱ	89.68 (5)	Cl1—U1—Cl1 ⁱ	180.000 (17)
O1 ⁱ —U1—Cl2 ⁱ	90.32 (5)	H1A—O1W—H1B	104 (6)
Cl2—U1—Cl2 ⁱ	180.000 (11)	H2A—N1—H2B	109.7 (14)

O1—U1—C11	89.86 (5)	H2A—N1—H2C	109.8 (14)
O1 ⁱ —U1—C11	90.13 (5)	H2B—N1—H2C	109.1 (14)
C12—U1—C11	91.145 (15)	H2A—N1—H2D	109.7 (14)
C12 ⁱ —U1—C11	88.855 (15)	H2B—N1—H2D	109.1 (14)
O1—U1—C11 ⁱ	90.14 (5)	H2C—N1—H2D	109.5 (14)

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

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>
O1w—H1A \cdots C11 ⁱⁱ	0.95 (6)	2.36 (7)	3.283 (2)	165 (7)
O1w—H1B \cdots C12 ⁱⁱⁱ	0.95 (5)	2.35 (5)	3.268 (2)	163 (5)
N1—H2A \cdots O1w	0.87 (3)	2.02 (3)	2.843 (2)	157 (3)
N1—H2B \cdots C11 ^{iv}	0.87 (4)	2.68 (4)	3.441 (2)	148 (3)
N1—H2C \cdots O1	0.87 (2)	2.32 (4)	3.014 (3)	137 (4)
N1—H2C \cdots C11 ^v	0.87 (2)	2.77 (3)	3.4060 (17)	131 (4)
N1—H2D \cdots O1w ^{vi}	0.87 (3)	2.03 (3)	2.887 (3)	169 (3)

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