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Bis(pyridinium) *trans*-tetrachloridodioxidouranate(VI) dioxane solvate

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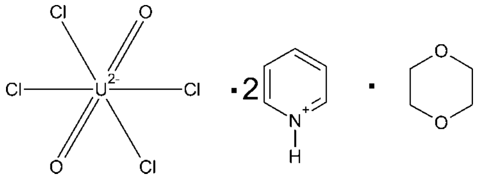
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.018 Å; R factor = 0.056; wR factor = 0.090; data-to-parameter ratio = 15.4.

In the crystal structure of the title compound, $(C_5H_6N)_2[UCl_4O_2]\cdot C_4H_8O_2$, the pyridinium cations occupy general positions and the anions and the solvent dioxane molecule are located on centres of inversion. The dioxane molecules are connected to two symmetry-related pyridinium cations *via* O—H···O hydrogen bonding. There are additional intermolecular C—H···Cl contacts, which are indicative of weak C—H···Cl interactions.

Related literature

For related literature, see Kaczmarek *et al.* (2004); Pospieszna-Markiewicz & Radecka-Paryzek (2004); Sessler *et al.* (2006); Allen (2002).



Experimental

Crystal data

$(C_5H_6N)_2[UCl_4O_2]\cdot C_4H_8O_2$
M_r = 660.15
Triclinic, $P\overline{1}$
a = 7.766 (2) Å
b = 8.666 (2) Å
c = 9.202 (2) Å
α = 63.57 (3)°
β = 67.08 (2)°
γ = 81.96 (2)°
V = 510.4 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 8.49 mm^{-1}
T = 100 (1) K
0.2 × 0.1 × 0.1 mm

Data collection

Kuma KM-4-CCD four-circle diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min}$ = 0.29, $T_{\max}$ = 0.43
3821 measured reflections
1770 independent reflections
1142 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.097

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.090
S = 0.89
1770 reflections
115 parameters
54 restraints
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.80 e Å^{-3}
$\Delta\rho_{\min}$ = −2.38 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.789 (7)	U1—Cl1	2.684 (3)
U1—Cl2	2.679 (3)		
O1—U1—Cl2	91.5 (2)	O1^{i}—U1—Cl1	91.6 (2)
O1^{i}—U1—Cl2	88.5 (2)	Cl2—U1—Cl1	89.43 (8)
Cl2^{i}—U1—Cl2	180	Cl2—U1—Cl1^{i}	90.57 (8)
O1—U1—Cl1	88.4 (2)	Cl1—U1—Cl1^{i}	180

Symmetry code: (i) $-x+2, -y+2, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C6B—H6B···Cl1	0.95	2.87	3.525 (12)	127
C2A—H2A2···Cl2^{ii}	0.99	2.88	3.754 (12)	147
N1B—H1B···O1A^{iii}	0.88	1.92	2.725 (11)	151
C4B—H4B···Cl1^{iv}	0.95	2.85	3.803 (13)	177

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2081).

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supporting information

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Bis(pyridinium) *trans*-tetrachloridodioxidouranate(VI) dioxane solvate

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S1. Comment

The use of uranium as a source of energy has caused increasing attention which is focused on the problem of fuel reprocessing and waste storage. Much effort has been devoted, in recent years, to the preparation and characterization of specific complexing agents for the uranyl ion (UO_2^{2+}), so-called "uranophiles" with the objective of a possible application for the separation of uranium species in waste liquids from the nuclear fuel cycle and for the recovery and utilization of uranium from the sea water (Sessler *et al.* 2006). The title compound was isolated during our study on the synthesis and characterization of uranyl complexes containing macrocyclic and acyclic polyaza and polyoxaaza Schiff bases derived from biogenic amines and their analogs to evaluate their potential as uranyl sequestering agents (Pospieszna-Markiewicz & Radecka-Paryzek, 2004; Kaczmarek *et al.*, 2004).

The asymmetric unit of the title compound (I) consists of one uranyl tetrachloride dianion and one dioxane molecule which are located on centres of inversion and one pyridinium cation which occupy a general position. This is quite common for similar complexes. In the Cambridge Structural Database (Allen, 2002; Version August 2007) there are 34 structures containing tetrachloro-uranyl dianions and a total of 144 structures which contain tetra-coordinated uranyl cations. Of those, 25 tetrachloro (79 for all) crystallizes with $Z'<1$, of which 22 (71 for all) have $Z'=1/2$.

In the crystal structure of the title compound the uranium atoms are coordinated by two oxygen and four chlorine atoms within slightly distorted octahedra (Fig. 1 and Tab.1). The U—O bond lengths of 1.789 (7)Å and the U—Cl bond lengths of 2.679 (3)Å and 2,684 (3)Å are close to the average CSD values (U—O = 1.77 (2)Å and U—Cl = 2.6791) Å, respectively).

Each two symmetry related pyridinium cations are connected by strong N—H···O hydrogen bonding to the dioxane molecule, forming hydrogen-bonded (pyridine···dioxane···pyridine)$^{2+}$ cations (Tab. 2). These building units are connected by weak C—H···Cl interactions to the dications into a three-dimensional network (Tab. 2 and Fig. 2).

S2. Experimental

The title compound was isolated during the slow diffusion of dioxane into pyridine hydrochloride solution of the uranyl(VI) Schiff base complex prepared through one-step template reaction of 2,6-diacetylpyridine with spermidine in the presence of uranyl(VI) acetateunder following conditions: to a mixture of uranyl acetate (42.5 mg, 0.1 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (16,3 mg, 0.1 mmol) in methanol (10 cm^3), spermidine (0.016 cm^3, 0.1 mmol) in methanol (10 cm^3) was added dropwise with stirring; the reaction wascarried out for 4 h, the solution volume was then reduced to 10 cm^3 by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether was filtered off, washed with ether, and dried *in vacuo*.

S3. Refinement

The H atoms were positioned with idealized geometry and were refined isotropic using a riding model with $U_{iso}(H) = 1.2$. U_{eq}(C,*N*) of the parent atom. Weak restraints (ISOR) were applied to the displacement parameters of C, N and O atoms.

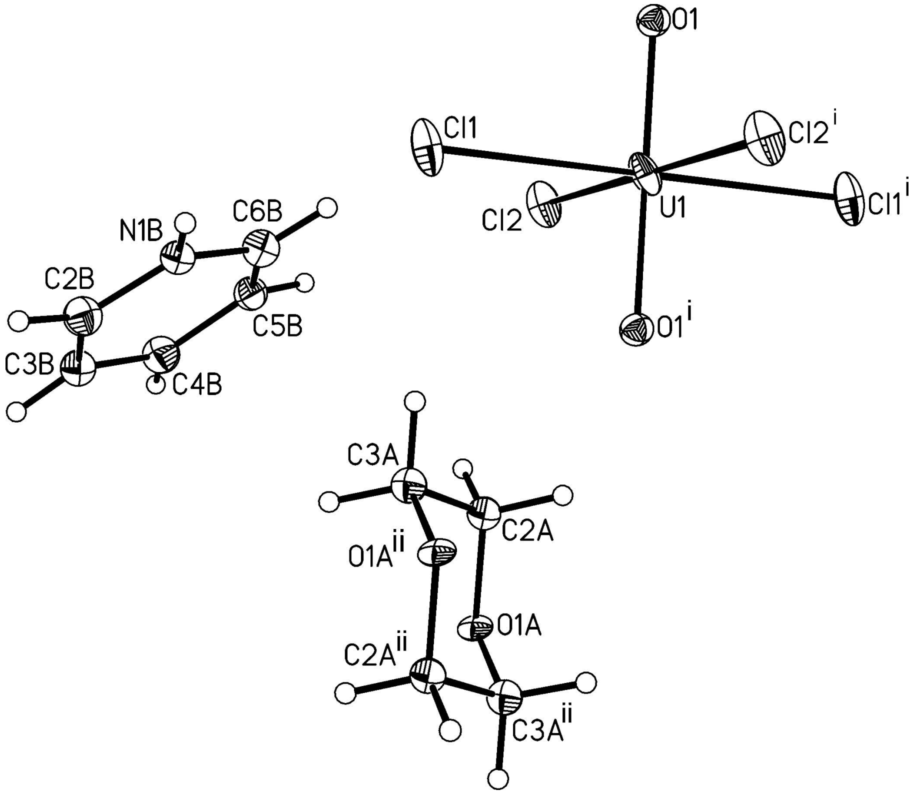

Figure 1

Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% propability level, H atoms are drawn as spheres with arbitrary radii. Symmetry codes: (i) 2 - *x*,2 - *y*,-*z*, (ii) 1 - *x*,1 - *y*,1 - *z*.

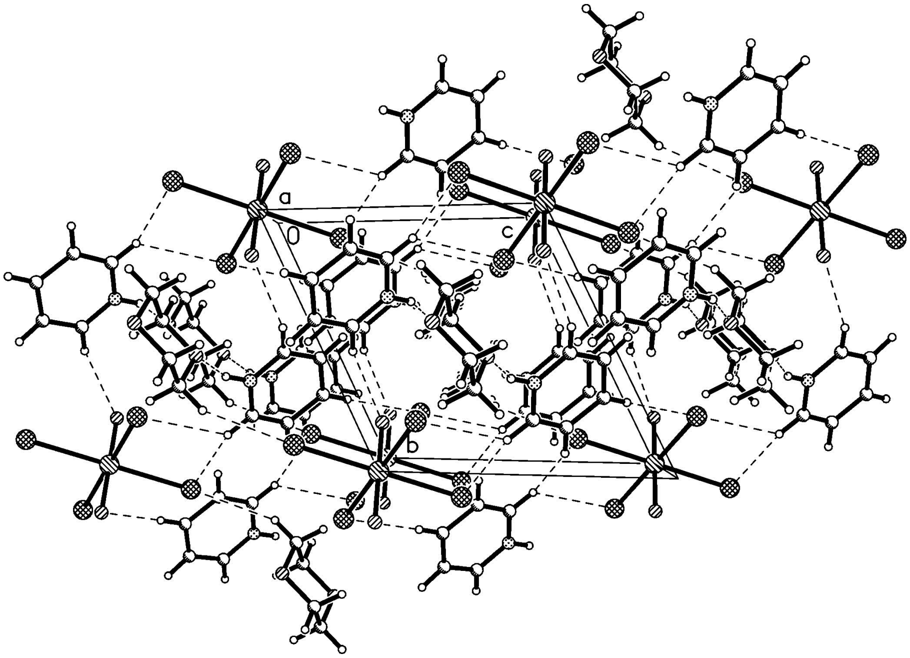

Figure 2

Crystal structure of (I) with view along the *a* axis. O—H···O hydrogen bonding and C—H···Cl interactions are shown as dashed lines.

bis(pyridinium) uranyl tetrachloridodioxidouranium(VI) dioxane solvate]

Crystal data

$(C_5H_6N)_2[UCl_4O_2]\cdot C_4H_8O_2$
M_r = 660.15
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.766 (2) Å
b = 8.666 (2) Å
c = 9.202 (2) Å
α = 63.57 (3)°
β = 67.08 (2)°
γ = 81.96 (2)°
V = 510.4 (3) Å^3

Z = 1
F(000) = 310
D_x = 2.148 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2368 reflections
θ = 4–25°
μ = 8.50 mm^{-1}
T = 100 K
Block, colourless
0.2 × 0.1 × 0.1 mm

Data collection

Kuma KM-4-CCD four-circle diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.29, T_{max} = 0.43

3821 measured reflections
1770 independent reflections
1142 reflections with $I > 2\sigma(I)$
R_{int} = 0.097
θ_{max} = 25.0°, θ_{min} = 2.6°
$h = -9\rightarrow8$
$k = -10\rightarrow9$
$l = -10\rightarrow5$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.090$
$S = 0.89$
1770 reflections
115 parameters
54 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.80$ e Å^{-3}
$\Delta\rho_{min} = -2.38$ 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.

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
U1	1.0000	1.0000	0.0000	0.0190 (3)
O1	0.8449 (10)	0.8196 (8)	0.0864 (8)	0.0147 (18)
Cl1	1.1731 (4)	0.8012 (3)	0.2188 (3)	0.0233 (9)
Cl2	0.7746 (4)	1.1044 (3)	0.2426 (3)	0.0220 (9)
O1A	0.3181 (10)	0.5610 (8)	0.5613 (8)	0.013 (2)
C2A	0.4823 (16)	0.6717 (13)	0.4704 (13)	0.017 (3)
H2A2	0.4632	0.7624	0.5122	0.022*
H2A1	0.5058	0.7287	0.3439	0.022*
C3A	0.6456 (17)	0.5718 (14)	0.4994 (13)	0.018 (3)
H3A2	0.7573	0.6508	0.4375	0.023*
H3A1	0.6230	0.5183	0.6256	0.023*
N1B	0.9618 (13)	0.6611 (10)	0.6810 (10)	0.016 (2)
H1B	1.0681	0.6435	0.6087	0.019*
C2B	0.9005 (17)	0.5495 (14)	0.8497 (13)	0.022 (3)
H2B	0.9733	0.4548	0.8923	0.027*
C3B	0.7294 (17)	0.5742 (14)	0.9614 (13)	0.020 (3)
H3B	0.6810	0.4911	1.0796	0.024*
C4B	0.6257 (18)	0.7202 (14)	0.9030 (13)	0.023 (3)
H4B	0.5107	0.7412	0.9792	0.028*
C5B	0.7038 (17)	0.8332 (14)	0.7241 (12)	0.018 (3)
H5B	0.6409	0.9347	0.6777	0.022*
C6B	0.8639 (17)	0.8001 (14)	0.6192 (14)	0.021 (3)
H6B	0.9103	0.8759	0.4983	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.0264 (6)	0.0098 (4)	0.0142 (4)	0.0037 (4)	−0.0084 (3)	0.0003 (3)
O1	0.015 (2)	0.015 (2)	0.015 (2)	0.0000 (10)	−0.0054 (11)	−0.0072 (11)
Cl1	0.031 (2)	0.0219 (17)	0.0137 (15)	0.0129 (17)	−0.0104 (16)	−0.0067 (13)
Cl2	0.026 (2)	0.0193 (17)	0.0173 (15)	0.0095 (16)	−0.0073 (15)	−0.0077 (13)
O1A	0.005 (5)	0.014 (4)	0.020 (4)	0.001 (4)	−0.004 (4)	−0.008 (3)
C2A	0.017 (3)	0.017 (3)	0.017 (3)	0.0005 (10)	−0.0060 (14)	−0.0072 (15)
C3A	0.018 (3)	0.018 (3)	0.018 (3)	0.0004 (10)	−0.0066 (14)	−0.0075 (15)
N1B	0.016 (2)	0.016 (2)	0.016 (2)	0.0006 (10)	−0.0053 (13)	−0.0073 (13)
C2B	0.022 (3)	0.022 (3)	0.022 (3)	0.0011 (10)	−0.0083 (15)	−0.0093 (15)
C3B	0.020 (3)	0.020 (3)	0.020 (3)	0.0009 (10)	−0.0076 (14)	−0.0082 (15)
C4B	0.023 (3)	0.023 (3)	0.023 (3)	0.0006 (10)	−0.0086 (15)	−0.0100 (16)
C5B	0.018 (3)	0.018 (3)	0.018 (3)	0.0008 (10)	−0.0067 (14)	−0.0078 (15)
C6B	0.021 (3)	0.021 (3)	0.021 (3)	0.0007 (10)	−0.0081 (14)	−0.0088 (15)

Geometric parameters (Å, º)

U1—O1	1.789 (7)	C3A—H3A1	0.9900
U1—O1^{i}	1.789 (7)	N1B—C2B	1.337 (11)
U1—Cl2^{i}	2.679 (3)	N1B—C6B	1.350 (12)
U1—Cl2	2.679 (3)	N1B—H1B	0.8800
U1—Cl1	2.684 (3)	C2B—C3B	1.386 (15)
U1—Cl1^{i}	2.684 (3)	C2B—H2B	0.9500
O1A—C2A	1.430 (13)	C3B—C4B	1.409 (13)
O1A—C3A^{ii}	1.440 (12)	C3B—H3B	0.9500
C2A—C3A	1.477 (13)	C4B—C5B	1.411 (12)
C2A—H2A2	0.9900	C4B—H4B	0.9500
C2A—H2A1	0.9900	C5B—C6B	1.331 (14)
C3A—O1A^{ii}	1.440 (12)	C5B—H5B	0.9500
C3A—H3A2	0.9900	C6B—H6B	0.9500
O1—U1—O1^{i}	180.000 (1)	O1A^{ii}—C3A—H3A2	109.2
O1—U1—Cl2^{i}	88.5 (2)	C2A—C3A—H3A2	109.2
O1^{i}—U1—Cl2^{i}	91.5 (2)	O1A^{ii}—C3A—H3A1	109.2
O1—U1—Cl2	91.5 (2)	C2A—C3A—H3A1	109.2
O1^{i}—U1—Cl2	88.5 (2)	H3A2—C3A—H3A1	107.9
Cl2^{i}—U1—Cl2	180.000 (1)	C2B—N1B—C6B	121.4 (10)
O1—U1—Cl1	88.4 (2)	C2B—N1B—H1B	119.3
O1^{i}—U1—Cl1	91.6 (2)	C6B—N1B—H1B	119.3
Cl2^{i}—U1—Cl1	90.57 (8)	N1B—C2B—C3B	119.0 (10)
Cl2—U1—Cl1	89.43 (8)	N1B—C2B—H2B	120.5
O1—U1—Cl1^{i}	91.6 (2)	C3B—C2B—H2B	120.5
O1^{i}—U1—Cl1^{i}	88.4 (2)	C2B—C3B—C4B	121.2 (10)
Cl2^{i}—U1—Cl1^{i}	89.43 (8)	C2B—C3B—H3B	119.4
Cl2—U1—Cl1^{i}	90.57 (8)	C4B—C3B—H3B	119.4
Cl1—U1—Cl1^{i}	180.000 (1)	C3B—C4B—C5B	115.7 (11)

C2A—O1A—C3A^{ii}	107.7 (8)	C3B—C4B—H4B	122.2
O1A—C2A—C3A	110.4 (8)	C5B—C4B—H4B	122.2
O1A—C2A—H2A2	109.6	C6B—C5B—C4B	121.2 (10)
C3A—C2A—H2A2	109.6	C6B—C5B—H5B	119.4
O1A—C2A—H2A1	109.6	C4B—C5B—H5B	119.4
C3A—C2A—H2A1	109.6	C5B—C6B—N1B	121.4 (10)
H2A2—C2A—H2A1	108.1	C5B—C6B—H6B	119.3
O1A^{ii}—C3A—C2A	112.1 (10)	N1B—C6B—H6B	119.3

Symmetry codes: (i) −*x*+2, −*y*+2, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6*B*—H6*B*···Cl1	0.95	2.87	3.525 (12)	127
C2*A*—H2*A*2···Cl2^{iii}	0.99	2.88	3.754 (12)	147
N1*B*—H1*B*···O1*A*^{iv}	0.88	1.92	2.725 (11)	151
C4*B*—H4*B*···Cl1^{v}	0.95	2.85	3.803 (13)	177

Symmetry codes: (iii) −*x*+1, −*y*+2, −*z*+1; (iv) *x*+1, *y*, *z*; (v) *x*−1, *y*, *z*+1.