

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(pyridinium) *trans*-tetrachlorido-dioxidouranate(VI) dioxane solvate

Izabela Pospieszna, Wanda Radecka-Paryzek and Maciej Kubicki*

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Correspondence e-mail: mkubicki@amu.edu.pl

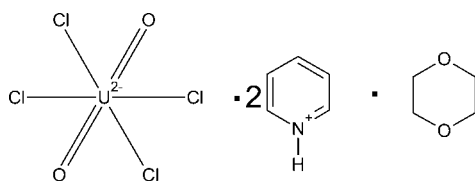
Received 16 November 2007; accepted 14 December 2007

 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.018$ Å; R factor = 0.056; wR factor = 0.090; data-to-parameter ratio = 15.4.

In the crystal structure of the title compound, $(\text{C}_5\text{H}_6\text{N})_2[\text{UCl}_4\text{O}_2] \cdot \text{C}_4\text{H}_8\text{O}_2$, 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* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonding. There are additional intermolecular $\text{C}-\text{H} \cdots \text{Cl}$ contacts, which are indicative of weak $\text{C}-\text{H} \cdots \text{Cl}$ 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

 $(\text{C}_5\text{H}_6\text{N})_2[\text{UCl}_4\text{O}_2] \cdot \text{C}_4\text{H}_8\text{O}_2$
 $M_r = 660.15$

 Triclinic, $P\bar{1}$
 $a = 7.766$ (2) Å

 $b = 8.666$ (2) Å

 $c = 9.202$ (2) Å

 $\alpha = 63.57$ (3)°

 $\beta = 67.08$ (2)°

 $\gamma = 81.96$ (2)°

 $V = 510.4$ (3) Å³
 $Z = 1$

 Mo $K\alpha$ radiation

 $\mu = 8.49$ mm⁻¹
 $T = 100$ (1) K

 $0.2 \times 0.1 \times 0.1$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.097$

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, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C6}B-H6B \cdots \text{Cl1}$	0.95	2.87	3.525 (12)	127
$\text{C2}A-H2A2 \cdots \text{Cl2}^{\text{ii}}$	0.99	2.88	3.754 (12)	147
$\text{N1}B-H1B \cdots \text{O1}A^{\text{iii}}$	0.88	1.92	2.725 (11)	151
$\text{C4}B-H4B \cdots \text{Cl1}^{\text{iv}}$	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*.

This work was supported by the Ministry of Science and Higher Education (grant No. N204 0317 33).

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

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Kaczmarek, M. T., Pospieszna-Markiewicz, I. & Radecka-Paryzek, W. (2004). *J. Includ. Phenom. Macrocyclic Chem.* **49**, 115–119.
- Oxford Diffraction (2006). *CrysAlis CCD* (Version 1.171.29.9) and *CrysAlis RED* (Version 1.171.29.9). Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Pospieszna-Markiewicz, I. & Radecka-Paryzek, W. (2004). *J. Alloys Compd.* **374**, 253–257.
- Sessler, J., Melfi, P. J. & Pantos, G. D. (2006). *Coord. Chem. Rev.* **250**, 816–843.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1989). *XP*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Acta Cryst. (2008). E64, m239 [doi:10.1107/S1600536807066949]

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

I. Pospieszna, W. Radecka-Paryzek and M. Kubicki

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

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) acetate under following conditions: to a mixture of uranyl acetate (42.5 mg, 0.1 mmol) in methanol (10 cm³) and 2,6-diacetylpyridine (16,3 mg, 0.1 mmol) in methanol (10 cm³), spermidine (0.016 cm³, 0.1 mmol) in methanol (10 cm³) was added dropwise with stirring; the reaction was carried out for 4 h, the solution volume was then reduced to 10 cm³ 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*.

Refinement

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

Figures

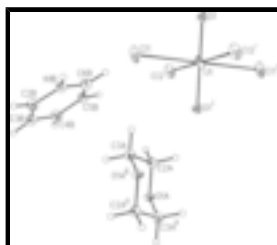


Fig. 1. Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level, H atoms are drawn as spheres with arbitrary radii. Symmetry codes: (i) $2 - x, 2 - y, -z$, (ii) $1 - x, 1 - y, 1 - z$.

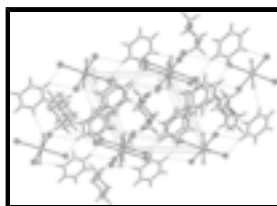


Fig. 2. Crystal structure of (I) with view along the a axis. O—H...O hydrogen bonding and C—H...Cl interactions are shown as dashed lines.

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

Crystal data

$(\text{C}_5\text{H}_6\text{N})_2[\text{UCl}_4\text{O}_2] \cdot \text{C}_4\text{H}_8\text{O}_2$

$M_r = 660.15$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.766\ (2)\ \text{\AA}$

$b = 8.666\ (2)\ \text{\AA}$

$c = 9.202\ (2)\ \text{\AA}$

$\alpha = 63.57\ (3)^\circ$

$\beta = 67.08\ (2)^\circ$

$\gamma = 81.96\ (2)^\circ$

$V = 510.4\ (3)\ \text{\AA}^3$

$Z = 1$

$F_{000} = 310$

$D_x = 2.148\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2368 reflections

$\theta = 4\text{--}25^\circ$

$\mu = 8.50\ \text{mm}^{-1}$

$T = 100\ (1)\ \text{K}$

Block, colourless

$0.2 \times 0.1 \times 0.1\ \text{mm}$

Data collection

Kuma KM-4-CCD four-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100\ (2)\ \text{K}$

ω scans

1770 independent reflections

1142 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.097$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 2.6^\circ$

Absorption correction: multi-scan
(CrysAlis RED; Oxford Diffraction, 2006) $h = -9 \rightarrow 8$
 $T_{\min} = 0.29, T_{\max} = 0.43$ $k = -10 \rightarrow 9$
 3821 measured reflections $l = -10 \rightarrow 5$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
$S = 0.89$	where $P = (F_o^2 + 2F_c^2)/3$
1770 reflections	$(\Delta/\sigma)_{\max} < 0.001$
115 parameters	$\Delta\rho_{\max} = 1.80 \text{ e } \text{\AA}^{-3}$
54 restraints	$\Delta\rho_{\min} = -2.38 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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*

supplementary materials

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

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—C12	88.5 (2)	H3A2—C3A—H3A1	107.9
C12 ⁱ —U1—C12	180.000 (1)	C2B—N1B—C6B	121.4 (10)
O1—U1—C11	88.4 (2)	C2B—N1B—H1B	119.3
O1 ⁱ —U1—C11	91.6 (2)	C6B—N1B—H1B	119.3
C12 ⁱ —U1—C11	90.57 (8)	N1B—C2B—C3B	119.0 (10)
C12—U1—C11	89.43 (8)	N1B—C2B—H2B	120.5
O1—U1—C11 ⁱ	91.6 (2)	C3B—C2B—H2B	120.5
O1 ⁱ —U1—C11 ⁱ	88.4 (2)	C2B—C3B—C4B	121.2 (10)
C12 ⁱ —U1—C11 ⁱ	89.43 (8)	C2B—C3B—H3B	119.4
C12—U1—C11 ⁱ	90.57 (8)	C4B—C3B—H3B	119.4
C11—U1—C11 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, °)

<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>
C6B—H6B \cdots C11	0.95	2.87	3.525 (12)	127
C2A—H2A2 \cdots C12 ⁱⁱⁱ	0.99	2.88	3.754 (12)	147
N1B—H1B \cdots O1A ^{iv}	0.88	1.92	2.725 (11)	151
C4B—H4B \cdots C11 ^v	0.95	2.85	3.803 (13)	177

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

Fig. 1

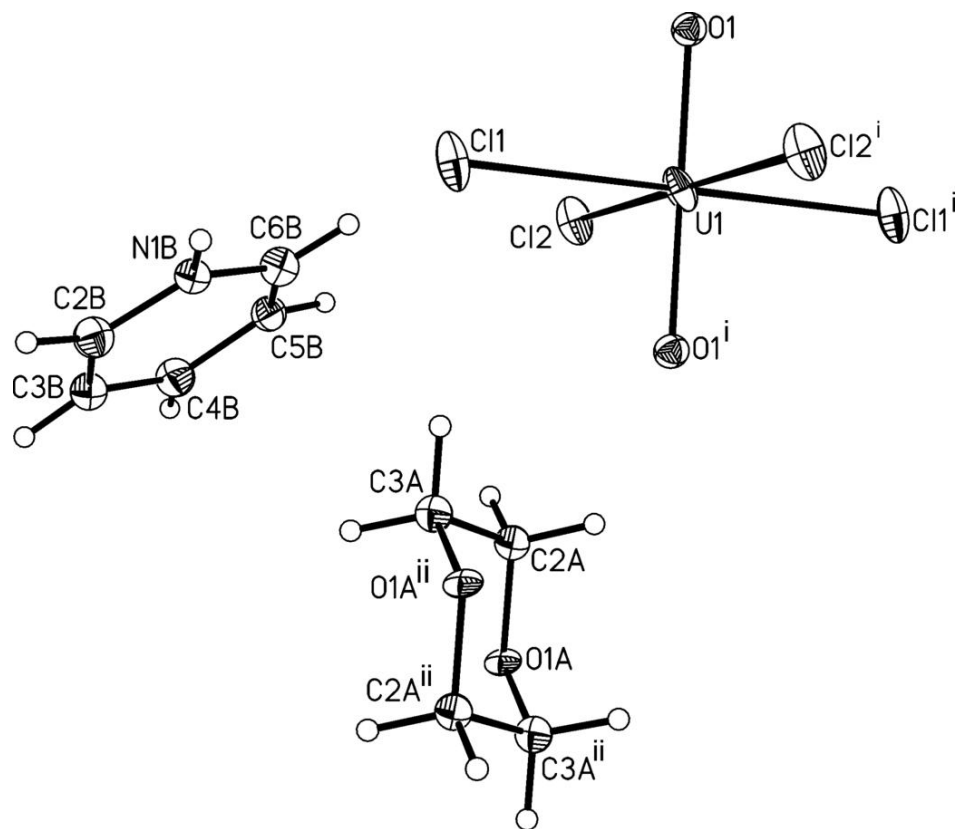


Fig. 2

