Acta Crystallographica Section C
Crystal Structure Communications

ISSN 0108-2701

π-Stacking and hydrogen bonding in *catena*-poly[[(4,4′-bipyridine-κN)-dioxouranium(VI)]-di-μ-hydroxo]

Pierre Thuéry

CEA/Saclay, DSM/DRECAM/SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France
Correspondence e-mail: pierre.thuery@cea.fr

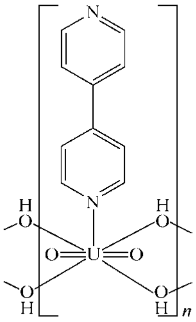
Received 6 December 2006
Accepted 14 December 2006
Online 23 January 2007

The title compound, $[UO_2(OH)_2(C_{10}H_8N_2)]_n$, was obtained under hydrothermal conditions. The U atom is seven-coordinated and its environment is pentagonal bipyramidal, with the oxo atoms in axial positions, and one N atom and four hydroxide groups in the equatorial plane. The hydroxide ions are bridging, which results in the formation of infinite chains with the bipyridine molecules alternately located on either side. Neighbouring chains interpenetrate so that each bipyridine ligand is involved both in hydrogen bonds with two hydroxide ions and in π-stacking with its two neighbours from the next chain.

Comment

Dioxouranium(VI) (uranyl) hydroxides and hydrates are known to organize as layered materials with the general formula $[(UO_2)_x(O)_y(OH)_z]\cdot nH_2O$ (Weller *et al.*, 2000). In particular, the α, β and γ forms of the polymorphic uranyl hydroxide $UO_2(OH)_2$, prepared under hydrothermal conditions, are composed of sheets in which the uranyl equatorial environment is either hexagonal or square planar (Roof *et al.*, 1964; Bannister & Taylor, 1970; Taylor, 1971; Taylor & Hurst, 1971; Siegel *et al.*, 1972). The complex $[UO_2(OH)_2(4,4'\text{-bipy})]$, (I), was also obtained under hydrothermal conditions, but coordination of the bipyridine molecule disrupts the planar arrangement of uranyl hydroxide to give an unusual one-dimensional polymer. It is to be noted that a search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) gives no example of 4,4′-bipyridine coordinated to the uranyl ion. The first examples were indeed reported recently in a family of uranyl complexes with aliphatic carboxylates formed in the presence of bipyridines (Borkowski & Cahill, 2006).

The asymmetric unit in (I) comprises one uranyl ion, two hydroxo groups and one monodentate 4,4′-bipyridine molecule (Fig. 1). A polymeric chain running along the *a* axis is formed through metal coordination to the images of the hydroxo groups generated by the helicoidal binary axis. The U atom is thus in the usual pentagonal–bipyramidal environment and is displaced by only 0.0242 (14) Å from the mean equatorial plane defined by atoms O3, O4, O3^{i}, O4^{i} and N1 [r.m.s. deviation 0.082 Å; symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$]. The average U1—O(oxo) and U1—O(μ-hydroxo) bond lengths are 1.795 (4) and 2.346 (4) Å, respectively (Table 1). The former is not significantly larger than the average value for comparable bonds found in the CSD [1.77 (3) Å, 738 structures], whereas the latter is in perfect agreement with the value of 2.34 (3) Å for double hydroxo bridges reported in the CSD (18 structures). It is to be noted that, whereas dinuclear uranyl complexes with a double hydroxide bridge are quite common, no example of a one-dimensional polymer based on this motif is present in the CSD. The U1—N1 bond length [2.614 (7) Å] is longer than the average value for the other U—N(4,4′-bipyridine) bonds reported [2.57 (2) Å; Borkowski



(I)

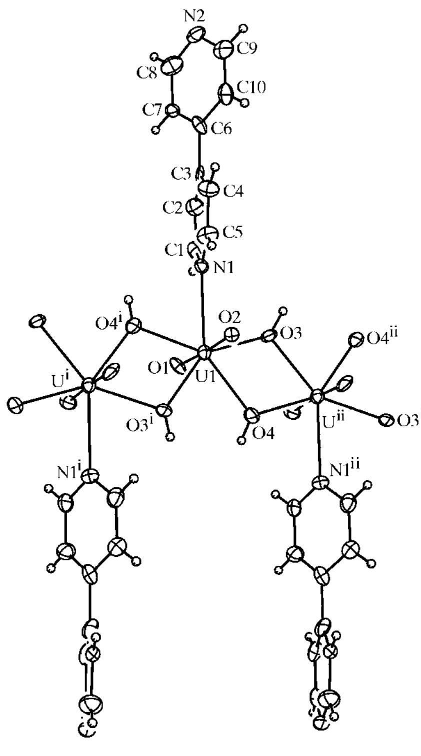


Figure 1
A view of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$.]

DOI: 10.1107/S0108270106054412

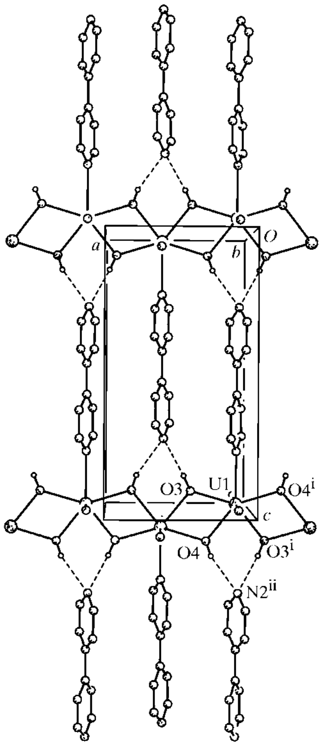


Figure 2
The packing through weak interactions in (I). Atoms are represented as spheres for clarity, C-bound H atoms have been omitted and hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (ii) $x, y, z + 1$.]

& Cahill, 2006]. The latter includes both mono- and bidentate bipyridines, but this does not seem to have an influence on the U—N bond lengths.

The chains directed along the *a* axis display successive 4,4′-bipyridine molecules pointing on either side along the *c* axis, which gives a planar double comb-like assemblage (Fig. 2). Neighbouring chains along the *c* axis interpenetrate in such a manner that the 4,4′-bipyridine molecules are roughly superimposable when viewed down the *a* axis, with a centroid offset of about 1.1 Å. The two aromatic rings in each molecule make a dihedral angle of 33.4 (2)°, but the coordinated (N1/C1–C5) and uncoordinated (N2/C6–C10) rings of neighbouring molecules are nearly parallel, with a dihedral angle of 2.9 (4)°. The presence of π-stacking interactions between these latter rings is indicated by the inter-centroid distances $Cg1\cdots Cg2^i$ = 3.838 Å and $Cg1\cdots Cg2^{ii}$ = 3.718 Å, where *Cg*1 and *Cg*2 are the centroids of the N1/C1–C5 and N2/C6–C10 rings, respectively [symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$] (the corresponding distances between planes are 3.48 and 3.60 Å, respectively). The shortest interatomic contacts are about 3.6 Å on either side, and thus slightly larger than twice the out-of-plane van der Waals radius of a C atom (1.7 Å; Bondi, 1964). These distances and offsets seem large, but they are compatible with the usual parallel-displaced stacking geometry (Meyer *et al.*, 2003). Further linking of neighbouring chains along the *c* axis is ensured by hydrogen bonds between the hydroxo groups and the uncoordinated N atoms (Table 2). All these weak interactions result in the formation of a two-dimensional framework parallel to the *ac* plane, in which ribbons of organic spacers and chains of uranyl hydroxide alternate. These sheets are superimposed along the *b* axis so that the projections of the U atoms of one sheet lie between the 4,4′-bipyridine molecules of the other, with no notable inter-sheet interactions, apart from van der Waals ones.

Experimental

Uranyl nitrate hexahydrate (135 mg, 0.269 mmol) and 4,4′-bipyridine (42 mg, 0.269 mmol) were dissolved in water (3 ml). The solution was placed in a tightly sealed vessel and heated at 453 K for two days under autogenous pressure. Crystals of (I) were formed during slow cooling of the solution.

Crystal data

$[UO_2(OH)_2(C_{10}H_8N_2)]$
M_r = 460.23
Orthorhombic, $P2_12_12_1$
a = 7.3964 (4) Å
b = 10.8144 (7) Å
c = 14.0800 (11) Å
V = 1126.23 (13) Å^3
Z = 4
D_x = 2.714 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 14.42 mm^{-1}
T = 110 (2) K
Irregular, translucent light yellow
0.10 × 0.10 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.213, T_{max} = 0.421
14902 measured reflections
2123 independent reflections
1901 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 25.7°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.086
S = 1.10
2123 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 4.3193P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.66 e Å^{-3}
$\Delta\rho_{min}$ = −1.41 e Å^{-3}
Absolute configuration: Flack (1983), 875 Friedel pairs
Flack parameter: 0.02 (3)

Table 1
Selected geometric parameters (Å, °).

U1—O1	1.799 (7)	U1—O3^i	2.343 (6)
U1—O2	1.790 (6)	U1—O4^i	2.343 (6)
U1—O3	2.353 (6)	U1—N1	2.614 (7)
U1—O4	2.345 (7)		
O1—U1—O2	175.9 (3)	O4^i—U1—N1	72.9 (2)
O3—U1—O4	68.4 (2)	N1—U1—O3	73.7 (2)
O4—U1—O3^i	76.7 (2)	U1—O3—U1^{ii}	111.2 (3)
O3^i—U1—O4^i	68.6 (2)	U1—O4—U1^{ii}	111.5 (3)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$\cdots$N2^{iii}	0.86	2.10	2.938 (11)	164
O4—H4$\cdots$N2^{iv}	0.80	2.26	3.015 (11)	159

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

H atoms bound to O atoms were found in a difference Fourier map and introduced as riding atoms, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(O). All other H atoms were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). The absolute configuration was determined from the value of the Flack (1983) parameter, which was refined together with the other parameters.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* (Bruker, 1999) and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3033). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bannister, M. J. & Taylor, J. C. (1970). *Acta Cryst.* B**26**, 1775–1781.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Borkowski, L. A. & Cahill, C. L. (2006). *Cryst. Growth Des.* **6**, 2248–2259.
Bruker (1999). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Meyer, E. A., Castellano, R. K. & Diederich, F. (2003). *Angew. Chem. Int. Ed.* **42**, 1210–1250.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Roof, R. B., Cromer, D. T. & Larson, A. C. (1964). *Acta Cryst.* **17**, 701–705.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Siegel, S., Hoekstra, H. R. & Gebert, E. (1972). *Acta Cryst.* B**28**, 3469–3473.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Taylor, J. C. (1971). *Acta Cryst.* B**27**, 1088–1091.
Taylor, J. C. & Hurst, H. J. (1971). *Acta Cryst.* B**27**, 2018–2022.
Weller, M. T., Light, M. E. & Gelbrich, T. (2000). *Acta Cryst.* B**56**, 577–583.