

Table 3. *Perpendicular displacements of the atoms from the least-squares plane of the porphinato core*

The equation of the plane is of the form: $-0.4741u - 0.4557v - 0.7543w + 15.4902 = 0$, where u, v, w are orthogonalized coordinates. Atoms with negative displacements are toward the pyrazine ring *F* side of the plane.

Distance (Å)		Distance (Å)	
Atoms in plane			
Fe	−0.031 (1)	C9	0.016 (5)
N1	0.020 (4)	C10	0.148 (5)
N2	−0.064 (4)	C11	0.109 (5)
N3	0.002 (4)	C12	0.146 (6)
N4	−0.048 (4)	C13	0.082 (6)
C1	0.124 (5)	C14	0.005 (5)
C2	0.239 (6)	C15	−0.025 (6)
C3	0.158 (6)	C16	0.086 (5)
C4	0.007 (5)	C17	−0.141 (6)
C5	−0.160 (5)	C18	−0.133 (6)
C6	−0.168 (5)	C19	−0.043 (5)
C7	−0.179 (6)	C20	0.059 (5)
C8	−0.038 (6)		
Other atoms			
N5	1.937 (4)	N7	−2.041 (4)
N6	4.722 (5)	N8	−4.864 (6)

ligands and the porphinato core, the planes of the two pyrazine ligands should be in superposition on the lines C5...C15 and C10...C20, respectively. Such an orientation allows a maximum and equidistant separation from the N and α -C atoms of the pyrrole rings. In the title compound these interactions are represented by the angles between the reference plane {C5, C15, Fe, N5, N7} and the planes {Fe, N5, C45} and {Fe, N7, C49}, which are 3.9 (1) and 37.0 (1)°. The latter two describe the planes of the pyrazine rings *E* and *F*, which make an angle of 40.9 (1)°. The corresponding values in TPPFe⁺(imidazole)₂ are 6, 63 and

57°. These values reflect that the pyrazine ring *F* is not well orientated to minimize steric repulsions and, consequently, the pyrrole rings *A* and *C* are displaced away from the atoms of that ligand. This steric repulsion might be responsible too for the stretched Fe—N7 bond length of 2.010 (3) Å compared with the distance $d(\text{Fe—N5}) = 1.970$ (3) Å.

References

- COLLINS, D. M., COUNTRYMAN, R. & HOARD, J. L. (1972). *J. Am. Chem. Soc.* **94**, 2066–2072.
- COLLMAN, J. P., HOARD, J. L., KIM, N., LANG, G. & REED, C. A. (1975). *J. Am. Chem. Soc.* **97**, 2676–2681.
- FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination*. In *Computing in Crystallography*, edited by H. SCHENCK, R. OLTROF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press. *SDP-Plus*, Version 1.1 (1984) and *VAXSDP*, Version 2.2 (1985).
- HANACK, M. (1983). *Chimia*, **37**, 238–245.
- HANACK, M. (1985). *Isr. J. Chem.* **25**, 205–209.
- International Tables for X-ray Crystallography* (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MEZGER, M. G. (1983). Thesis. Univ. of Tübingen.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- RADONOVICH, L. J., BLOOM, A. & HOARD, J. L. (1972). *J. Am. Chem. Soc.* **94**, 2073–2078.
- SCHEIDT, W. R. (1977). *Acc. Chem. Res.* **10**, 339–345.
- STEFFEN, W. L., REED, C. A., SAYLER, A. A. & HOARD, J. L. (1987). In preparation.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1987). **C43**, 1267–1269

Actinide Structural Studies. 12.* 4,4'-Bipyridinium Di- μ -hydroxo-bis[dinitratodioxouranate(VI)] Monohydrate

BY N. W. ALCOCK AND D. J. FLANDERS

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

(Received 20 September 1986; accepted 18 March 1987)

Abstract. $[\text{C}_{10}\text{H}_{10}\text{N}_2][\text{U}_2\text{O}_4(\text{OH})_2(\text{NO}_3)_4] \cdot \text{H}_2\text{O}$, $M_r = 998.3$, monoclinic, Pn , $a = 13.336$ (3), $b = 5.555$ (2), $c = 15.433$ (3) Å, $\beta = 94.25$ (1)°, $V = 1140.1$ (5) Å³, $Z = 2$, $D_x = 2.91$, $D_m = 2.85$ (2) g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 135.5$ cm⁻¹, $F(000) = 904$, $T =$

290 K, $R = 0.026$ for 1920 unique observed $[I/\sigma(I) \geq 3.0]$ reflections. The hydroxy-bridged anion contains uranyl groups [U—O 1.785 (14) Å] equatorially coordinated by two bidentate NO₃⁻ groups [U—O 2.52 (2) Å] and two hydroxide groups [U—O 2.36 (3) Å]. The bipyridinium anions are slightly twisted about the central C—C bond [dihedral angle

* Part 11: Alcock & Roberts (1987).

6.3 (1)°. The ions are linked by a network of hydrogen bonds.

Introduction. This part of our study of actinide structures was undertaken as an extension of our work on complexes of 2,2'-bipyridyl (Alcock, Flanders & Brown, 1985) to complexes involving 4,4'-bipyridyl. It was also of potential interest in comparison to previous studies on 4,4'-bipyridyl complexes of lanthanide nitrates (Weakley, 1982).

Experimental. Following the previously reported preparation of UO₂(NO₃)₂·1.5(4,4'-bipyridyl) (Ahuja & Singh, 1973), uranyl nitrate hexahydrate (0.5 mmol) and excess 4,4'-bipyridyl (2.5 mmol) were reacted in hot ethanol (5 cm³) to give a yellow amorphous product. This proved very difficult to recrystallize and the only solvent in which the powder dissolved was water. The yellow plates obtained had a different infrared spectrum to that of the original product, but this spectrum suggested that the 4,4'-bipyridyl group was still present in the crystalline material and a structure determination was carried out.

Data were collected with a Syntex P₂ four-circle diffractometer. Maximum 2θ was 50°, with scan range -1.0, +1.1° (2θ) around the Kα₁-Kα₂ angles, scan speed 2-29° min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.5 of the scan time. *hkl* ranges were: 0→15; 0→6; -18→18. Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Density was measured by flotation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections (20 < 2θ < 24°). Reflections were processed using profile analysis to give 2342 unique reflections; 1920 were considered observed [*I*/σ(*I*) ≥ 3.0] and used in the refinement; they were corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970); maximum and minimum transmission factors were 0.65 and 0.50. Crystal dimensions were 0.11 × 0.29 × 0.05 mm, with bounding faces: $\bar{1}01$, $10\bar{1}$; {001}, 021, 02 $\bar{1}$. Systematic absence: *h*0 \bar{l} , *h* ≠ 2*n* indicates space groups *P*2/*n* or *Pn*. One U atom was initially located by Patterson methods in *P*2/*n*, but satisfactory light-atom positions could only be found in *Pn*; this space group was confirmed by the satisfactory refinement. The light atoms were found on successive Fourier syntheses, including one solvent H₂O. Anisotropic temperature factors were used for all non-H atoms except the O of this water molecule. H atoms were given fixed isotropic temperature factors, *U* = 0.07 Å², inserted at calculated positions and not refined (omitting those of the H₂O and the bridging OH). The absolute structure of the individual crystal chosen was checked by refinement of an *f''* multiplier

Table 1. Atom coordinates (× 10⁴) and isotropic temperature factors (Å² × 10³)

	x	y	z	U _{eq} /U
U(1)	3628.5	1648.4 (9)	4844.0	18 (1)*
U(2)	6371.7 (5)	4319.6 (9)	5159.1 (5)	20 (1)*
O(001)	5278 (21)	2348 (48)	2651 (17)	133 (9)
O(1)	4856 (10)	4162 (17)	4269 (8)	20 (4)*
O(2)	5139 (11)	1750 (21)	5711 (9)	32 (5)*
O(11)	3172 (11)	4234 (25)	5351 (10)	39 (5)*
O(12)	4086 (8)	-1005 (23)	4335 (8)	37 (4)*
O(13)	3159 (10)	3298 (26)	3365 (8)	48 (4)*
O(14)	1988 (11)	1367 (22)	3904 (8)	29 (4)*
O(15)	1762 (10)	2722 (24)	2583 (7)	45 (4)*
O(16)	2195 (8)	-683 (21)	5428 (7)	36 (4)*
O(17)	3511 (8)	-485 (25)	6275 (8)	43 (4)*
O(18)	2197 (9)	-2422 (26)	6693 (7)	43 (4)*
N(11)	2283 (11)	2375 (30)	3267 (9)	35 (5)*
N(12)	2623 (11)	-1271 (25)	6142 (8)	31 (4)*
O(21)	6863 (13)	1786 (20)	4617 (11)	42 (5)*
O(22)	5891 (9)	6855 (19)	5713 (7)	33 (4)*
O(23)	6916 (10)	2314 (23)	6555 (8)	42 (4)*
O(24)	8032 (11)	4645 (31)	6036 (11)	54 (6)*
O(25)	8385 (10)	2488 (28)	7256 (8)	54 (5)*
O(26)	7789 (9)	6702 (25)	4573 (8)	42 (4)*
O(27)	6413 (9)	6629 (23)	3719 (8)	42 (4)*
O(28)	7715 (10)	8426 (24)	3296 (9)	51 (5)*
N(21)	7801 (11)	3085 (25)	6645 (12)	34 (5)*
N(22)	7332 (11)	7297 (27)	3831 (10)	40 (5)*
N(3)	4916 (12)	3326 (25)	7397 (8)	35 (5)*
N(4)	5108 (12)	9327 (28)	11381 (10)	42 (5)*
C(1)	5556 (15)	2525 (35)	8051 (11)	42 (6)*
C(2)	5569 (12)	3591 (32)	8842 (11)	34 (5)*
C(3)	4945 (12)	5565 (29)	8971 (11)	31 (5)*
C(4)	4308 (14)	6284 (32)	8288 (11)	35 (5)*
C(5)	4334 (15)	5132 (40)	7460 (14)	51 (7)*
C(6)	4977 (12)	6805 (31)	9842 (10)	25 (5)*
C(7)	5597 (13)	6051 (32)	10533 (9)	33 (5)*
C(8)	5644 (15)	7285 (36)	11298 (12)	45 (6)*
C(9)	4507 (16)	10154 (38)	10729 (12)	48 (7)*
C(10)	4416 (13)	8987 (33)	9939 (10)	36 (5)*

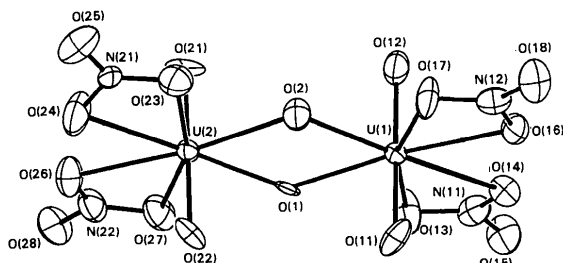
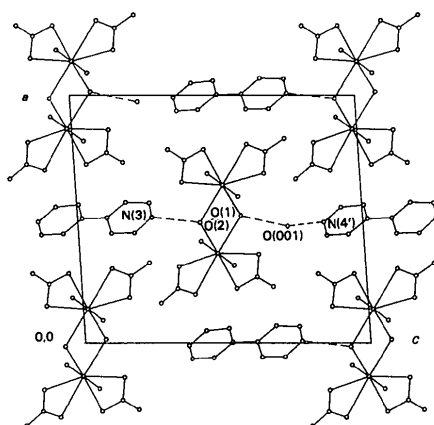
* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

but the refined value -0.09 (4) shows no discrimination. An extinction parameter (Sheldrick, 1983) refined to the value 0.00032 (2). The *x* and *z* coordinates of U(1) were fixed to define the origin. Final refinement was on *F* by cascaded least-squares methods refining 329 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height +1.5 and -0.9 e Å⁻³; all the large peaks were ripples around U. A weighting scheme of the form *w* = 1/[σ(*F*)²] was used and shown to be satisfactory by a weight analysis. Final *R* = *wR* = 0.026. Maximum shift/e.s.d. in final cycle 0.2. Computing with *SHELXTL* (Sheldrick, 1983) on a Data General DG30. Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates are given in Table 1, and selected bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43819 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Principal bond lengths (Å) and angles (°)

	n=1	n=2		n=1	n=2
U(n)—O(1)	2.37 (1)	2.36 (1)	U(n)—O(n3)	2.50 (1)	2.49 (1)
U(n)—O(2)	2.34 (1)	2.38 (1)	U(n)—O(n4)	2.54 (1)	2.51 (2)
U(n)—O(n1)	1.77 (1)	1.79 (1)	U(n)—O(n6)	2.53 (1)	2.53 (1)
U(n)—O(n2)	1.80 (1)	1.79 (1)	U(n)—O(n7)	2.52 (1)	2.57 (1)
U(1)—O(n)—U(2)	112.9 (5)	113.5 (5)	O(n1)—U(n)—O(n2)	179.4 (6)	179.3 (4)

Fig. 1. View of the $[\text{UO}_2(\text{OH})(\text{NO}_3)_2]^{2-}$ ion, showing the atomic numbering.Fig. 2. Projection of the structure down **b** with hydrogen bonds dashed.

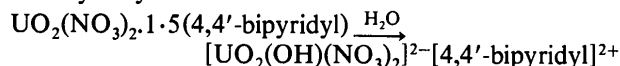
Discussion. The compound formed in the recrystallization consists of di- μ -hydroxo-bis[dinitratodioxouranate(VI)] anions, 4,4'-bipyridinium cations and water molecules and Fig. 1 shows the structure of the anion. The two dioxouranium(VI) groups are bonded by the bridging hydroxide groups so that the U atoms are at the centres of neighbouring hexagonal bipyramids with one common edge. The mean U—O distance in the uranyl groups is 1.785 (14) Å and the mean U—O ligand distances are 2.52 (2) Å for nitrate and 2.36 (3) Å for hydroxide. The axial UO_2 groups are almost perfectly linear $[\text{O}—\text{U}—\text{O}] 179.3 (5)^\circ$, and the

equatorial ligands have little puckering [range of $\text{O}_{\text{ax}}—\text{U}—\text{O}_{\text{eq}}$ angles $86.3 (6)–92.5 (5)^\circ$].

The view of the cell (Fig. 2) down the *b* axis shows the arrangement of the ion pairs. The bipyridinium ion is slightly twisted about the C—C bond between the two rings, with a dihedral angle of $6.3 (1)^\circ$. The structure is held together in chains (Fig. 2) parallel to *c* by hydrogen bonds from the water molecule $[\text{O}(001) \cdots \text{O}(1) 2.79 (2)$; $\text{O}(001) \cdots \text{N}(4')(\text{translated along } c) 2.58 (2) \text{ Å}]$ and between N(3) and O(2) $[2.78 (2) \text{ Å}]$.

A number of O-bridged uranyl species are known, but only two μ -OH species are included in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). The most relevant structure is that of the choline salt of the same anion as that reported here (Viossat, Nguyen-Huy Dung & Soye, 1983). The anion is identical in overall geometry to the present one, except that it is centrosymmetric, and both the bridging and terminal equatorial U—O distances are similar $[2.34 (1) \text{ and } 2.55 (2) \text{ Å}]$. However, the U—O(axial) distances are surprisingly short $[1.706 (10) \text{ Å, mean}]$. The second structure determination involves the $[\{\text{UO}_2(\text{H}_2\text{O})_3\}_2(\text{OH})_2]^{2+}$ cation (Navaza, Villain & Charpin, 1984); its slightly shorter U—O distances are understandable both in terms of the charge and of the five rather than six equatorial ligands $[\text{U}—\text{O}(\text{bridging}) 2.29 (2), \text{U}—\text{O}(\text{H}_2\text{O}) 2.45 (2), \text{U}—\text{O}(\text{axial}) 1.72 (2) \text{ Å}]$.

A hydrolysis reaction of the form:



appears to be responsible for the formation of the ionic material, but the mechanism has not been determined. The presence of bipyridyl may well be important both to provide cations and to control the pH, to produce this unexpected partly hydrolysed uranyl nitrate anion.

References

- AHUJA, L. S. & SINGH, R. (1973). *Aust. J. Chem.* **26**, 1871–1876.
- ALCOCK, N. W. (1970). *Crystallographic Computing*, edited by F. R. AHMED, pp. 271–278. Copenhagen: Munksgaard.
- ALCOCK, N. W., FLANDERS, D. J. & BROWN, D. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1001–1007.
- ALCOCK, N. W. & ROBERTS, M. M. (1987). *Acta Cryst.* **C43**, 476–478.
- ALLEN, F. H., KENNARD, O. & TAYLOR, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- NAVAZA, A., VILLAIN, F. & CHARPIN, P. (1984). *Polyhedron*, **3**, 143–149.
- SHELDRIK, G. M. (1983). *SHELXTL Users Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin.
- VIOSAT, B., NGUYEN-HUY DUNG & SOYE, C. (1983). *Acta Cryst.* **C39**, 573–576.
- WEAKLEY, T. J. R. (1982). *Inorg. Chim. Acta*, **63**, 161–168.