is clear from the figures and tables that – as a comparison of the structures of (1) and (2) indicates – no interaction between C(10) and C(20) occurs. The observed kinetic phenomenon would therefore appear to be an effect only in the transition state of the elimination (i).

It has been spectroscopically established (Laube, 1984) that in the isolated molecules (in solution) the perpendicular orientation of the two phenyl rings with respect to the plane defined by square-planar Pt valences is the preferred conformation with a relatively deep potential hollow; as a consequence E, Z isomers of bis-*ortho*-substituted compounds have been detected (Laube, 1984). In the solid phase the phenyl rings in (1) and (2) deviate from this perpendicular orientation [81·9 and 86·9° in (1); 82·8 and 81·1° in (2)]; these distortions are probably caused by packing effects due to short intermolecular distances.

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Actinide Structural Studies. 11.* X-ray Study of a Possible Seven-Coordinate Uranyl Ion: Structure of (2,2'-Bipyridine *N,N'*-dioxide)dinitratodioxouranium(VI)

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Abstract. $[UO_2(NO_3)_2(C_{10}H_8N_2O_2)]$, $M_r = 582\cdot2$, monoclinic, $P2_1/c$, $a = 9\cdot231$ (5), $b = 10\cdot556$ (7), $c = 15\cdot839$ (5) Å, $\beta = 96\cdot99$ (4)°, $V = 1532$ (1) Å^3, $Z = 4$, $D_x = 2\cdot52$, $D_m = 2\cdot3$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 101\cdot1$ cm^{-1}, $F(000) = 1072$, $T = 291$ K, $R = 0\cdot063$ for 1974 unique observed reflections. The title compound contains a $[UO_2]^{2+}$ ion [U–O 1·76 (2) Å], coordinated by one 2,2'-bipyridine *N,N'*-dioxide [U–O 2·38 (1) Å] and two NO_3^- groups [U–O 2·51 (1) Å]. Evidence is presented that the supposed seven-coordinate $[UO_2]^{2+}$ ion in $[UO_2(bpyO_2)_2-(NO_3)_2].4H_2O$ in reality exists as the six-coordinate $[UO_2(bpyO_2)_2(NO_3)]^+$ ion.

Introduction. A complex formed from uranyl nitrate and 2,2'-bipyridine *N,N'*-dioxide (bpyO$_2$) was claimed by Madan & Chan (1977) from IR evidence to contain $[UO_2]^{2+}$ ions coordinated by seven equatorial ligands, made up of two bidentate bpyO$_2$ groups, one bidentate and one unidentate nitrate. However, this conclusion seems suspect in view of the steric constraints around the $[UO_2]^{2+}$ group, where even six ligands can only be

fitted in if one or more short-bite bidentate ligands are present (Alcock, 1973). Furthermore, the identification of precisely how nitrate groups are coordinated from their IR spectrum is known to be uncertain (Cotton, Goodgame & Sonderberg, 1963). Two complexes can be formed in this system, depending on the precise preparative conditions: $[UO_2(bpyO_2)(NO_3)_2]$ (1) (previously prepared by Ahuja & Singh, 1973) and $[UO_2(bpyO_2)_2(NO_3)_2].4H_2O$ (2) (as reported by Madan & Chan, 1977) and these have been investigated crystallographically.

Experimental. The preparative conditions for (1) and (2) are almost identical, except that for (1) the solution of bpyO$_2$ is reacted with solid uranyl nitrate, whereas (2) is formed from solutions of the reactants.

(1) was prepared by adding a solution of 2,2'-bipyridine *N,N'*-dioxide (8·5 mmol) in hot methanol (400 ml) to uranyl nitrate hexahydrate (4·2 mmol) in the solid state. The reaction mixture yielded a fine precipitate of the desired product on standing for a few hours. Crystals of a suitable size for X-ray diffraction studies were obtained by slow evaporation from a hot glacial acetic acid solution. The IR spectrum and the formula as obtained from X-ray structure analysis agree with those reported by Ahuja & Singh (1973).

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(2) was prepared by adding 2,2'-bipyridine N,N'-dioxide (8·5 mmol) in hot methanol (400 ml) to uranyl nitrate hexahydrate (4·2 mmol) in cold methanol (40 ml). This gave a clear yellow solution from which crystals were obtained by slow evaporation. Again, the IR spectrum agrees with that previously reported (Madan & Chan, 1977).

For (1): crystal character: yellow laths. Data collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ 55°, with scan range $\pm 1\cdot0°$ (2θ) around the $K\alpha_1 - K\alpha_2$ angles, scan speed 1–29° min^{-1}, depending on the intensity of a 2 s pre-scan; background measured at each end of the scan for 0·25 of the scan time. hkl ranges: 0–11; 0–13; −19–20. Three standard reflections monitored every 100 reflections, and showed no changes during data collection. Density measured by flotation. Unit-cell dimensions and standard deviations obtained by least-squares fit to 15 reflections. Reflections processed to give 3942 unique reflections; 1974 considered observed $[I/\sigma(I) \geq 3\cdot0]$ and used in refinement; corrected for Lorentz, polarization and absorption effects, the last with $ABSCOR$ (Alcock, 1970); maximum and minimum transmission factors 0·42 and 0·38. Crystals dimensions 0·12 × 0·18 × 0·40 mm. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$ indicate space group $P2_1/c$. Heavy atom located by Patterson interpretation and the light atoms then found on successive Fourier syntheses. Anisotropic temperature factors for all non-H atoms. H atoms given fixed isotropic temperature factors, $B = 4\cdot7$ Å^2 and not refined. Final refinement by least squares based on F; weighting scheme $W = X.Y$, where $X = 1\cdot0$ or $\sin\theta/0\cdot30$ for $\sin\theta \leq 0\cdot30$ and $Y = 1\cdot0$ or $90\cdot0/F_o$ for $F_o \geq 90\cdot0$. Final $R = 0\cdot063$; $wR = 0\cdot072$. The final difference Fourier map showed residual peaks <5 e Å^{-3} close to the U atom, and < 2 e Å^{-3} elsewhere. Maximum shift to e.s.d. in final cycle 0·37. Computing with $XRAY76$ (Stewart, 1976) on a Burroughs B6800. 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 bond lengths and angles in Table 2.*

The crystals of (2) were handled identically to those of (1). They were apparently monoclinic, with $a = 14\cdot136$ (3), $b = 8\cdot218$ (2), $c = 12\cdot881$ (2) Å, $\beta = 113\cdot90$ (1)°, $V = 1368\cdot0$ (5) Å^3. For $C_{20}H_{24}N_6O_{16}U$, $M_r = 842\cdot4$, $D_x = 2\cdot04$ g cm^{-3} for $Z = 2$, $\mu = 57\cdot1$ cm^{-1}, $F(000) = 812$. 4842 reflections collected to $2\theta = 63°$ [3423 with $I/\sigma(I) \geq 3\cdot0$]. Transmission factors: 0·44 to 0·19. Systematic absence $0k0$, $k \neq 2n$.

Table 1. *Atomic coordinates* ($\times 10^4$) *with standard deviations in parentheses and average isotropic U values*

	x	y	z	$U(Å^2)$
U	2272·5 (8)	55·8 (8)	2332·3 (4)	30
O(1)	588 (15)	124 (17)	1052 (8)	41
O(2)	1028 (19)	−1880 (13)	2088 (8)	39
O(5)	958 (18)	461 (15)	3002 (10)	46
O(6)	3569 (17)	−356 (16)	1648 (10)	50
O(11)	4137 (20)	48 (19)	3641 (10)	55
O(12)	5003 (21)	−1612 (20)	4342 (12)	65
O(13)	3241 (20)	−1767 (15)	3292 (10)	49
O(21)	1932 (23)	2205 (17)	1696 (12)	62
O(22)	3134 (32)	3899 (17)	2143 (13)	83
O(23)	3692 (22)	2030 (16)	2692 (12)	57
N(1)	4177 (23)	−1096 (21)	3774 (12)	49
N(2)	2944 (30)	2781 (20)	2190 (14)	61
N(3)	−800 (19)	−256 (18)	1004 (9)	36
N(4)	1170 (21)	−2521 (16)	1350 (11)	37
C(1)	−1850 (32)	589 (27)	1131 (18)	55
C(2)	−3292 (29)	206 (30)	984 (18)	60
C(3)	−3667 (30)	−1018 (27)	727 (17)	54
C(4)	−2522 (26)	−1883 (23)	623 (15)	44
C(5)	−1084 (23)	−1489 (21)	774 (13)	37
C(6)	105 (23)	−2378 (21)	685 (12)	36
C(7)	2295 (32)	−3291 (23)	1335 (15)	52
C(8)	2404 (28)	−4044 (27)	618 (17)	53
C(9)	1354 (31)	−3908 (26)	−78 (15)	53
C(10)	191 (36)	−3069 (23)	−62 (18)	46

indicated space groups $P2_1$ or $P2_1/m$. The U position was obtained from a Patterson synthesis [in special position $2(e)$, with m symmetry in $P2_1/m$ or in a general position in $P2_1$]; refinement in $P2_1/m$ gave unreasonable contact between ligand atoms across the mirror plane, and was abandoned. In $P2_1$, a structure was obtained, with a $[UO_2]^{2+}$ group six-coordinated by two (bpyO$_2$) groups and one bidentate NO$_3^-$. This could be refined to $R = 0\cdot047$, but showed two unsatisfactory features: (1) the absence of a second NO$_3^-$ group (presumably uncoordinated), (2) an unacceptably short contact between a C atom of one cation and an O of another. Extensive attempts to discover an alternative resolution of the false symmetry imposed by the U atom produced no improvement, and it was concluded that the crystals were probably twinned in an unidentified manner. However, the cation seen, although clearly not positioned correctly in the cell, seems very likely to be a true image of the cation in compound (2).

Discussion. Complex (1) displays hexagonal bipyramidal coordination about U (Fig. 1) resulting from two uranyl O atoms, a bidentate bpyO$_2$ and two bidentate nitrate groups. The U–O(NO$_3$) bonds (2·49–2·55 Å) are somewhat longer than the U–O(bpyO$_2$) bonds (2·35–2·40 Å), though they are similar to other bonds to bidentate NO$_3^-$, e.g. in [UO$_2$(triphenylphosphine oxide)$_2$(NO$_3$)$_2$] (Alcock, Roberts & Brown, 1982). The chelating 'bites' in both nitrates are 2·13 (3) Å, which is characteristic of this group in actinyl complexes. However, the O$\cdots$O 'bite' in the bpyO$_2$ ligand [2·68 (3) Å] is comparable to the non-

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* (1) *with standard deviations in parentheses*

(a) Bond lengths
(i) Around U

U—O(1)	2·402 (12)	U—O(11)	2·528 (15)
U—O(2)	2·354 (14)	U—O(13)	2·546 (16)
U—O(5)	1·758 (17)	U—O(21)	2·487 (18)
U—O(6)	1·764 (17)	U—O(23)	2·490 (18)

(ii) Bipyridine *N,N'*-dioxide rings

O(1)—N(3)	1·336 (23)	O(2)—N(4)	1·370 (22)
N(3)—C(1)	1·350 (35)	N(4)—C(6)	1·359 (25)
C(1)—C(2)	1·384 (40)	C(6)—C(10)	1·400 (34)
C(2)—C(3)	1·386 (42)	C(10)—C(9)	1·394 (41)
C(3)—C(4)	1·421 (37)	C(9)—C(8)	1·384 (34)
C(4)—C(5)	1·384 (31)	C(8)—C(7)	1·400 (37)
C(5)—N(3)	1·368 (28)	C(7)—N(4)	1·321 (33)
C(5)—C(6)	1·465 (31)		

(iii) Nitrate groups

N(1)—O(11)	1·225 (30)	N(2)—O(21)	1·295 (30)
N(1)—O(12)	1·232 (27)	N(2)—O(22)	1·196 (28)
N(1)—O(13)	1·292 (26)	N(2)—O(23)	1·266 (28)

(b) Bond angles
(i) Around U

O(1)—U—O(2)	68·5 (5)	O(23)—U—O(21)	50·7 (6)
O(2)—U—O(13)	64·6 (5)	O(21)—U—O(1)	66·0 (6)
O(13)—U—O(11)	49·7 (6)	O(5)—U—O(6)	179·1 (7)
O(11)—U—O(23)	61·9 (6)		

(ii) Bipyridine *N,N'*-dioxide rings

O(1)—N(3)—C(5)	116·9 (18)	N(4)—C(6)—C(5)	118·4 (18)
O(1)—N(3)—C(1)	119·6 (20)	N(4)—C(6)—C(10)	119·1 (21)
N(3)—C(1)—C(2)	118·4 (25)	C(6)—C(10)—C(9)	118·0 (24)
C(1)—C(2)—C(3)	121·5 (27)	C(10)—C(9)—C(8)	121·2 (24)
C(2)—C(3)—C(4)	118·1 (24)	C(9)—C(8)—C(7)	118·3 (25)
C(3)—C(4)—C(5)	119·8 (22)	C(8)—C(7)—N(4)	119·9 (22)
C(4)—C(5)—C(6)	120·3 (20)	C(7)—N(4)—C(6)	123·4 (19)
C(4)—C(5)—N(3)	118·7 (20)	C(7)—N(4)—O(2)	118·4 (17)
O(2)—N(4)—C(6)	118·1 (18)		

(iii) Nitrate groups

O(11)—N(1)—O(12)	124·3 (20)	O(21)—N(2)—O(22)	121·7 (23)
O(12)—N(1)—O(13)	119·9 (21)	O(22)—N(2)—O(23)	125·7 (24)
O(13)—N(1)—O(11)	115·8 (18)	O(23)—N(2)—O(21)	112·5 (19)

(iv) Subtended by donor O atoms

U—O(1)—N(3)	123·8 (10)	U—O(13)—N(1)	95·7 (12)
U—O(2)—N(4)	118·3 (12)	U—O(21)—N(2)	97·9 (13)
U—O(11)—N(1)	98·5 (13)	U—O(23)—N(2)	98·6 (14)

Fig. 1. View of molecule (1) [UO$_2$(bpyO$_2$)(NO$_3$)$_2$], showing the atomic numbering.

bonded O···O separations in many uranyl complexes, indicating that the only constraints are due to van der Waals forces. For both the bpyO$_2$ O atoms to coordinate, though, it is necessary for the two pyridyl rings to assume a twisted conformation relative to each other. This results in a dihedral angle of 53·7 (5)° between the rings. This same twisted conformation of bpyO$_2$ is found in the structure of [La(bpyO$_2$)$_4$(ClO$_4$)$_3$] (Al-Karaghouli, Day & Wood, 1978), although there it is more exaggerated (61·4°). That complex consists of an almost cubic arrangement of eight coordinated O atoms about La. Consequently, non-bonded O···O interactions are less likely than in the hexagonal bipyramidal form of (1), and correspondingly the bpyO$_2$ 'bite' is larger [2·801 (4) Å, av.].

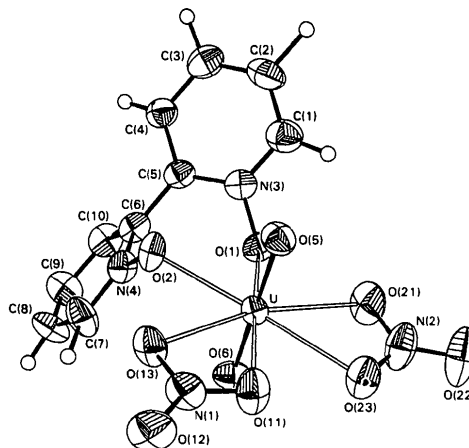Although the crystallographic study of (2) could not be completed, it has given a strong indication that (2)

contains the [UO$_2$(bpyO$_2$)$_2$(NO$_3$)]$^+$ ion, *i.e.* with a six-coordinate [UO$_2$]$^{2+}$ ion. This would indicate that the IR study (Madan & Chan, 1977) was correct in recognizing two different NO$_3^-$ absorptions in the spectrum, but failed to identify their bonding modes. The additional evidence from the same source that in solution the species is a non-electrolyte, suggests that under the conditions used, an equilibrium is set up between (2) and (1)

$$[UO_2(bpyO_2)_2(NO_3)]^+(NO_3)^- \rightleftharpoons [UO_2(bpyO_2)\text{-}(NO_3)_2] + bpyO_2$$
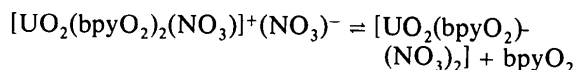
and that this equilibrium lies to the right, though presumably the addition of bpyO$_2$ would increase the concentration of (2).

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