Actinide Structural Studies. Part 6.[1] A Confirmed Non-linear Uranyl Group in Dioxobis(pentane-2,4-dionato)pyridineuranium(VI) †

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The crystal structure of the title compound has been determined using *X*-ray diffraction methods. The complex exhibits pentagonal-bipyramidal co-ordination involving two bidentate pentane-2,4-dionate ions and a pyridine molecule about the uranyl(VI) ion. The metal–ligand oxygen distances are 2.34(1) and 2.44(1) Å, the metal–ligand nitrogen distance is 2.47(1) Å, and the U–O (UO_2^{2+}) distances are 1.83(1) Å. The bond angle O–U–O (UO_2^{2+}) is 173.5(8)°, confirming the non-linearity previously suggested from spectroscopic evidence. The crystals are orthorhombic, space group *Fdd*2, with $a = 29.702(4)$, $b = 11.433(2)$, $c = 10.593(2)$ Å, and $Z = 8$. The structure has been refined to an *R* value of 0.032 using 832 observed, diffractometer-measured intensities.

A large number of complexes of dioxouranium(VI) with pyridine and its derivatives has been reported[2] but in the majority of cases the only investigations carried out have been of the i.r. spectra, usually involving the identification of ν_{asym}(OUO) and ν_{sym}(OUO). The title compound was reported in 1927[3] and i.r. data were obtained later.[4,5] Interpretation of these data in the light of theoretical calculations[6] led to the conclusion that the O–U–O uranyl(VI) group was not linear. We have now determined the structure from single-crystal *X*-ray data and demonstrated that this group is indeed significantly bent.

Experimental

The compound was prepared following the method of Hager,[3] and formed crystals immediately. These were recrystallised from methanol. A number of crystals had to be examined to obtain a suitable single crystal for structure determination as the majority were twinned.

Infrared spectra were taken with a Perkin-Elmer 180 spectrophotometer using Nujol mulls between KBr plates for the region 1 000—400 cm^{-1} and between silicon plates for the region 500—150 cm^{-1}. These confirmed the spectra obtained previously;[4,5] the expected absorption at *ca.* 210 cm^{-1} (characterised[5] as ν_2) was observed at 235 cm^{-1}.

Crystallography.—Crystal data. $C_{15}H_{19}NO_6U$, $M = 549.38$, orthorhombic, space group *Fdd*2, $a = 29.702(4)$, $b = 11.433(2)$, $c = 10.593(2)$ Å, $U = 3\,597.3(10)$ Å^3, $D_m = 2.03$ g cm^{-3}, $Z = 8$, $D_c = 2.02$, Mo-K_α radiation, graphite monochromator, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 85.8 cm^{-1}, $F(000) = 2\,064$.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 55°, with scan range ±1.05 (2θ) around the $K_{\alpha1}$–$K_{\alpha2}$ angles and scan speed 1.5—29.0° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections monitored every 200 reflections showed slight but systematic changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Of 1 173 reflections collected 832 were deemed to be observed [$I/\sigma(I) > 3.0$] and were used in subsequent refinement. They were corrected for Lorentz polarisation, and absorption effects, the last with ABSCOR;[7] maximum and minimum transmission factors were 0.57 and 0.28 respectively. Crystal dimensions were 0.30 × 0.30 × 0.18 mm. The systematic absences (hkl: $h + k, k + l \neq 2n$; $0kl$: $k + l \neq 4n$; $h0l$: $h + l \neq 4n$) indicated space group *Fdd*2. A further strong pseudo absence (hkl: $h + k + l \neq 2n + 1$ or $4n$) suggested that the uranium atom was in special position 8*a* with two-fold site symmetry. Successive Fourier syntheses with the uranium placed at 0,0,0 (*z* arbitrarily chosen and fixed as 0) located the light atoms around the uranium. Hydrogen atoms were inserted at calculated positions with fixed isotropic thermal parameters, $B = 5.0$ Å^2, and were not refined. Final refinement was carried out by the least-squares method, with a weighting scheme of the form $W = XY$, where $X = 1.0$ or $(\sin\theta/\lambda)/0.35$ for $(\sin\theta/\lambda) < 0.35$ or $0.99/(\sin\theta/\lambda)$ for $(\sin\theta/\lambda) > 0.99$, and $Y = 1.0$ or $600.0/F$ for $F > 600.0$. This was shown to be satisfactory by a weighting analysis. The final *R* value was 0.032. Refinement with the opposite-handed molecule led to an increase in *R*. The hand originally used is therefore taken to be correct.

Calculations were carried out with the *X*-RAY 76 system,[8] on a Burroughs B6700 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 9.

Final atomic co-ordinates are given in Table 1, bond lengths and angles in Table 2, and details of least-squares planes in Table 3. Views of the molecule and the unit cell are given in Figures 1 and 2.

Results and Discussion

The compound exhibits pentagonal-bipyramidal co-ordination about the uranium atom involving two bidentate pentane-2,4-dionate ions and a pyridine molecule about the uranyl(VI) ion. Thus it has a similar geometry to uranyl(VI) bis(pentane-2,4-dionate) hydrate, the only other uranyl pentane-2,4-dionate complex to have been studied structurally.[10] However, closer comparison is not possible due to the relatively low accuracy of the latter determination. The ligand dimensions in the complex are normal, as are the equatorial uranium–ligand distances; U–N is somewhat longer than the average U–O (equatorial), as expected from the covalent radii. However, the uranyl(VI) group itself is very unusual. It has significantly longer U–O distances [1.83(1) Å] than is usual (*ca.* 1.75 Å)[11] for complexes with five equatorial ligands and the O–U–O angle [173.5(8)°] deviates considerably from linearity. This might be due to packing effects, but the complex shows no close intermolecular interactions involving O(1) and as Figure

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† *Supplementary data available* (No. SUP 23831, 8 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Atomic co-ordinates ($\times 10^4$), with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	0	0	0	C(8)	−925(7)	−1 317(22)	3 348(18)
N(1)	0	0	−2 334(13)	H(1)	42	−1 743	−2 633
O(1)	−425(4)	1 158(10)	97(17)	H(2)	4	−1 812	−4 809
O(2)	524(4)	1 393(13)	−668(13)	H(3)	0	0	−6 126
O(3)	376(4)	821(12)	1 846(12)	H(41)	1 392	2 023	−1 745
C(1)	19(7)	−1 012(12)	−2 992(14)	H(42)	969	2 944	−1 782
C(2)	13(10)	−1 040(19)	−4 319(15)	H(43)	1 332	3 135	−785
C(3)	0	0	−5 184(15)	H(6)	1 320	2 061	1 253
C(4)	1 151(6)	2 562(20)	−1 145(17)	H(81)	1 195	1 608	3 233
C(5)	886(5)	1 834(14)	−214(18)	H(82)	−797	−703	3 986
C(6)	1 026(6)	1 777(18)	1 044(18)	H(83)	−990	−1 977	4 074
C(7)	760(5)	1 306(15)	2 010(17)				

Table 2. Important bond lengths (Å) and angles (°), with standard deviations in parentheses *

U-O(1)	1.83(1)	C(4)-C(5)	1.51(3)
U-O(2)	2.34(1)	C(5)-O(2)	1.28(2)
U-O(3)	2.44(1)	C(5)-C(6)	1.40(3)
U-N(1)	2.47(1)	C(6)-C(7)	1.40(3)
		C(7)-O(3)	1.28(2)
N(1)-C(1)	1.35(2)	C(7)-C(8)	1.50(3)
C(1)-C(2)	1.41(2)		
C(2)-C(3)	1.50(2)		
O(1)-U-O(1′)	173.5(8)	C(4)-C(5)-C(6)	120(2)
O(2)-U-O(3)	71.1(4)	C(4)-C(5)-O(2)	114(2)
O(2)-U-N(1)	72.4(3)	C(6)-C(5)-O(2)	126(2)
O(2)-U-O(2′)	144.7(5)	C(5)-C(6)-C(7)	123(2)
O(3)-U-O(3′)	73.4(4)	C(6)-C(7)-C(8)	120(2)
O(1)-U-O(2)	89.1(5)	C(6)-C(7)-O(3)	125(2)
O(1)-U-O(3)	89.6(6)	C(8)-C(7)-O(3)	115(2)
O(1)-U-N(1)	93.2(5)		
		C(1)-N(1)-C(1′)	118(1)
		N(1)-C(1)-C(2)	122(1)
		C(1)-C(2)-C(3)	126(2)
		C(2)-C(3)-C(2′)	105(1)
		C(1)-N(1)-U	121(1)

* Primed atoms are related to unprimed ones by a two-fold axis.

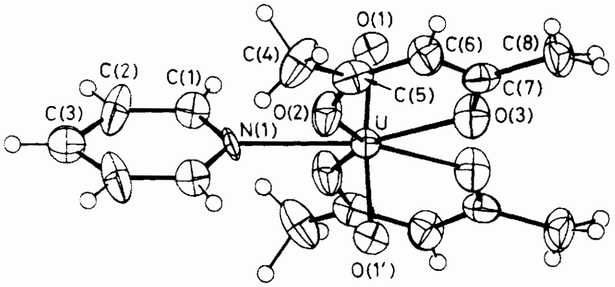

Figure 1. View of the molecule showing the atomic numbering. O(1′) is related to O(1) by the two-fold axis

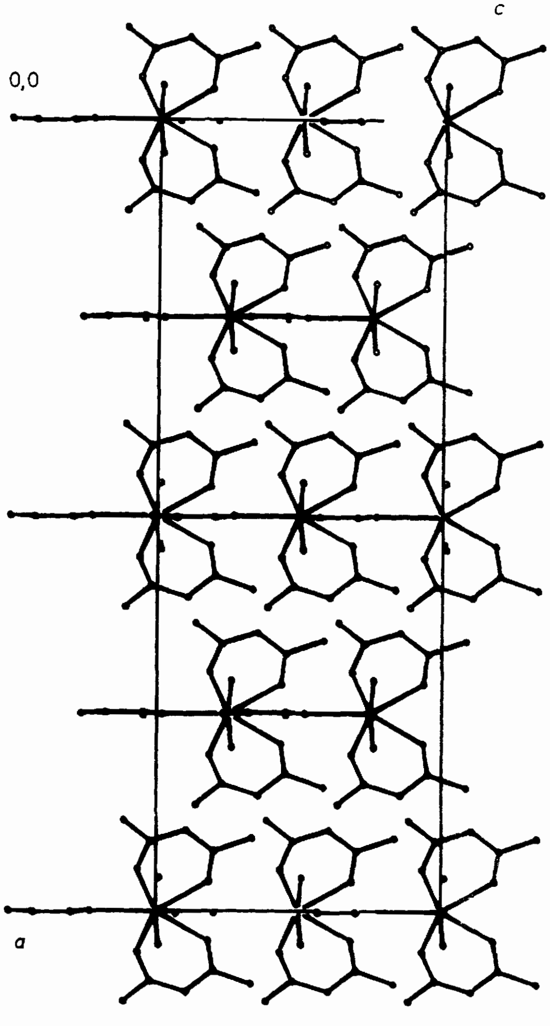

Figure 2. Packing diagram, viewed down *b*

2 illustrates, the main contacts are between pentane-2,4-dionate groups. The direction of the bend in the O-U-O group is more informative (Figure 1). This group is very clearly bent away from the pyridine substituent, as is confirmed by the N(1)-U-O(1) angle of 93.2(5)°, deviating from 90° by almost precisely half the deviation of the O-U-O angle from 180°. Furthermore the pyridine ring is twisted by 45° out of the equatorial plane, presumably to avoid interference with the pentane-2,4-dionate groups. This must, however, increase repulsions between the *ortho*-hydrogen atoms on the pyridine and the uranyl oxygen atoms, and must be responsible for the observed bent O-U-O group. It presumably also causes the unusually long U-O distance, although the lengthening seems somewhat large for the degree of bending observed. Also of significance is that the deviation of 6.5° from linearity is sufficient to produce the observed spectroscopic effects.

A number of other examples of bent uranyl(VI) groups has been reported, but consideration of those listed in a recent

Table 3. Deviations (Å) from mean planes (defined by starred atoms) †

Plane
1 U* 0.02, O(2)* 0.03, O(2′)* 0.06, O(3)* −0.06, O(3′)* −0.08, N(1)* 0.03
2 U* 0.00, N(1)* 0.00, C(1)* 0.06, C(1′)* −0.06, C(2)* 0.04, C(2′) * −0.04, C(3)* 0.00

Line
3 O(1)* 0.05, U* 0.00, O(1′)* 0.05

Angles (°) between planes and between line 3 and normals to planes
1–2 44.6, 1–3 4.8, 2–3 45.8

† Primed atoms are related to unprimed ones by a two-fold axis.

review,[12] coupled with a study of the later literature, shows that the majority occur in polymerised systems. Only three have been found with bond angles < 175° in monomeric systems. Of these, uranyl diperchlorate heptahydrate [13] with a uranyl(VI) bond angle of 161(3)° should hardly be considered, as it contains extensive hydrogen bonding involving the uranyl(VI) oxygens. [3-Oxapentane-1,5-diyl-*N*,*N*′-bis-(salicylideneiminato)]dioxouranium(VI) [14] exists in two crystal modifications, each with a bent uranyl(VI) group [174.2(6) and 173.8(5)°]. Infrared and Raman spectral data again show the expected absorptions for non-linear uranyl(VI) groups. These groups do not, however, have abnormal U–O bond lengths. Clearly the deviations from linearity in these structures must also be of intramolecular origin, and an interaction is suggested with two oxygen atoms in the equatorial girdle, which are forced by the molecular geometry to have short U–O distances (mean 2.20 *vs.* 2.34—2.44 Å in the title compound).

The final example, dioxobis(8-quinolinolato)(8-quinolinol)-uranium(VI) [15] has a reported O–U–O angle of 174.8°. The standard deviation is unstated, but may be as large as ±2°, and so the reality of the deviation from linearity is not fully established. However, the molecular geometry is rather similar to that of the bis(salicylidene) derivative and the cause may be the same.

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