Preparation, Properties, and Crystal Structure of Tetraethylammonium Bis(1,3-diphenylpropane-1,3-dionato)nitratodioxouranate(VI)

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The title complex has been synthesized and characterized. The crystal structure has been determined by *X*-ray analysis from counter data, and refined to *R* 0.052 for 2 085 observed reflections. Crystals are orthorhombic, space group $Pn2_1a$, with $a = 20.384(9)$, $b = 14.543(5)$, $c = 12.641(5)$ Å, and $Z = 4$. The approximately linear uranyl group is perpendicular to the equatorial plane in which four oxygen atoms from two bidentate diketonate ligands and the oxygen atom of the unidentate nitrate group occupy the corners of a quasi-regular pentagon. The structure is also discussed on the basis of i.r. and n.m.r. measurements.

THE preparations and physicochemical properties of a large series of neutral β-ketoenolate complexes of the uranyl ion have been reported. Although the complexes can be obtained anhydrous,[1-3] their crystalline form usually contains one molecule of a variety of neutral N- or O-donor ligands, giving mononuclear five-coordinate species.[4-6] The electronic, i.r., and ^{1}H n.m.r. spectra of these species have been studied and some correlations between different physical parameters have been attempted, in order to evaluate the donor ability of the various neutral ligands.[1,3,6-11] Much work has been done on the use of neutral ligands as synergists in the solvent extraction of uranyl ion with β-diketones.[9,10,12-17]

We have investigated the reactions between neutral uranyl β-diketonates and anionic ligands, and obtained a new class of anionic complexes of formula $[UO_2(\text{diketonate})_2X]^-$. This paper describes the preparation, characterization, and *X*-ray structure of the complex $[NEt_4][UO_2(dppd)_2(NO_3)]$ (dppd = 1,3-diphenylpropane-1,3-dionate); a complete investigation of the whole series of anionic complexes will be presented elsewhere.

EXPERIMENTAL

Materials.—Reagent-grade uranyl acetate dihydrate, 1,3-diphenylpropane-1,3-dione, and tetraethylammonium nitrate (Fluka products) were used without further purification. Methanol and ethyl acetate, used as solvents, were distilled before use. Acetonitrile was carefully purified as reported in the literature.[18]

Preparation of Tetraethylammonium Bis(1,3-*diphenylpropane*-1,3-*dionato*)*nitratodioxouranate*(VI).—1,3-Diphenylpropane-1,3-dione (5.2 mmol) in methanol (10 cm^3) at 60 °C was added to $[UO_2(O_2CMe)_2]\cdot 2H_2O$ (2.6 mmol) in water (40 cm^3) also at 60 °C. After 1 h on a water-bath the mixture was allowed to cool. The crystals of $[UO_2(dppd)_2(OH_2)]$ which formed were filtered off and dried in air. To $[UO_2(dppd)_2(OH_2)]$ (0.145 g, 0.2 mmol) dissolved in ethyl acetate (10 cm^3) containing a few drops of methanol was added a methanolic solution (3 cm^3) of $[NEt_4][NO_3]$ (0.038 g, 0.2 mmol) with stirring. The resulting solution was allowed to concentrate on standing in air. Brilliant orange crystals slowly formed and were separated, washed with a little ethyl acetate, and dried in air, m.p. 278—280 °C (Found: C, 49.95; H, 4.40; N, 3.05; U, 26.1. $C_{38}H_{42}N_2O_9U$ requires C, 50.2; H, 4.60; H, 3.10; U, 26.2%). Uranium was determined gravimetrically as the tetraphenylarsonium salt of dioxobis(pyridine-2,6-dicarboxylato)uranate(VI).[19] The complex is relatively soluble in acetonitrile, slightly soluble in acetone and chloroform, and practically insoluble in water.

Physical Measurements.—The molar conductivity at 25 °C was measured on 10^{-3} mol dm^{-3} solutions of the complex in acetonitrile using an LKB 3216B conductivity bridge. Infrared spectra (400—4 000 cm^{-1}) were recorded for KBr disks on a Perkin-Elmer 621 spectrophotometer; far-i.r. spectra (80—400 cm^{-1}) were obtained as Nujol mulls between polyethylene plates using a Beckman 11 instrument. Hydrogen-1 n.m.r. spectra for solutions in acetonitrile were recorded on a Varian T60 spectrometer using $SiMe_4$ as internal standard. Electronic spectra (230—650 nm) for solutions in acetonitrile were obtained on a Hitachi EPS-3T double-beam spectrophotometer using 1-cm quartz cells. The results obtained are shown in Table 1.

Crystal Data.—$C_{38}H_{42}N_2O_9U$, Red prisms, orthorhombic, $M = 908.8$, $a = 20.384(9)$, $b = 14.543(5)$, $c = 12.641(5)$ Å,

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U = 3 747 Å^3, D_m = 1.61 g cm^{-3} (flotation), Z = 4, D_c = 1.61 g cm^{-3}. Space group $Pn2_1a$ (C_{2v}^9) from systematic absences $hk0$ ($h \neq 2n$) and $0kl$ ($k + l \neq 2n$). Mo-K_α radiation: μ(Mo-K_α) = 65.5 cm^{-1}, λ = 0.710 7 Å.

Table 1

Physical data for the complex $[NEt_4][UO_2(dppd)_2(NO_3)]$

Λ/S cm^2 mol^{-1}	143
$\lambda_{max.}$/nm	259(sh), 278, 337, 397
I.r. bands (cm^{-1})	1 589s, 1 537vs, 1 519vs, 1 477s, 1 449s, 1 440sh, 1 392m, 1 383s, 1 368s, 1 353m, 1 313m, 1 290s, 1 224m, 1 183w, 1 173w, 1 157w, 1 122w, 1 094w, 1 063m,br, 1 031m, 1 020m, 999m, 940m, 900vs, 818w,br, 785m, 768m, 720s, 696m, 686ms, 617w, 602m, 518m, 448w, 425w, 352w, 269w, 255w
^{1}H n.m.r. spectrum (δ/p.p.m.)	8.63(m, 4 H, *o*-H of 2 Ph), 7.67-(m, 6 H, *m*- and *p*-H of 2 Ph), 7.42(s, 2 H, vinyl H)

A well formed prismatic single crystal of dimensions *ca.* 0.1 × 0.2 × 0.1 mm was mounted on a glass fibre with epoxy adhesive. A Philips PW 1100 single-crystal diffractometer was used with graphite-monochromated Mo-K_α radiation. The unit-cell parameters were determined by a least-squares refinement of the angular settings of 25 reflections. The diffracted intensities of 3 076 independent reflections were collected by the ω—2θ technique with $2 < \theta < 25°$, and 2 085 of these having $I > 3\sigma(I)$ were used in the structure determination and refinement. All the data were corrected for Lorentz and polarization effects but not for absorption.

Determination of the structure. Scattering factors for neutral atoms were taken from Cromer and Waber.[20] The uranium scattering factor was corrected for anomalous dispersion using constant average values of $\Delta f' = -9.19$ and $\Delta f'' = 9.09$ for the real and imaginary components. The systematic absences are compatible with space groups $Pn2_1a$ (C_{2v}^9) and $Pnma$ (D_{2h}^{16}). The cell parameters and density indicated four molecules per unit cell which is compatible with a general position in $Pn2_1a$ but which in $Pnma$ requires molecular site symmetry C_i (which must be excluded on chemical grounds) or C_s which was excluded when it was evident that the plane of the molecule is neither coplanar with nor perpendicular to the crystallographic mirror; hence the non-centric space group $Pn2_1a$ was adopted and confirmed during the course of the study. The relative positions of the uranium atoms were obtained from a sharpened Patterson function, and subsequent difference-Fourier maps revealed the positions of all the remaining non-hydrogen atoms. Atomic positions were refined by least-squares minimization of the function $\Sigma\omega(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors and the weights (ω) were unity. Refinement was then continued with individual anisotropic temperature factors for all atoms except those of the phenyl rings and converged at $R[= \Sigma(|F_o| - |F_c|)K/\Sigma|F_o|]$ 0.052 when the maximum shift of the variable positional parameters was 0.4σ. The structure of the molecule and its position with respect to (010) excludes, as expected, the presence of a mirror plane, but the possibility of a disordered structure compatible with space group $Pnma$ was not discarded in principle. An alternative refinement was then carried out in this space group with U, 0(5), N(2), C(31), and C(35) lying on the mirror plane at y = 0.25, and assuming for each of the other atoms two symmetrically related positions at opposite sides of the mirror plane having an occupancy of 0.5. Four cycles of refinement including anisotropy for these atoms reduced R to 0.074. At convergence the co-ordinates of the atoms were approximately the same as in space group $Pn2_1a$, but the uranyl bond lengths and some carbon–carbon distances of the phenyl rings were clearly unreliable. Thus it was confirmed that the space group was $Pn2_1a$.

Table 2

Fractional co-ordinates (× 10^4) with estimated standard deviations

Atom	*x*	*y*	*z*
U	1 245(0)	2 500	570(1)
O(1)	1 721(13)	3 970(15)	1 011(16)
O(2)	1 389(10)	3 419(13)	−962(15)
O(3)	867(12)	1 132(15)	1 265(16)
O(4)	782(11)	1 660(14)	−802(14)
O(5)	1 348(22)	2 674(14)	2 502(25)
O(6)	482(10)	3 057(12)	753(13)
O(7)	2 019(10)	2 034(14)	326(15)
O(8)	1 211(24)	2 311(86)	4 051(27)
O(9)	1 967(15)	1 756(26)	3 026(36)
N(1)	1 511(16)	2 233(30)	3 236(20)
N(2)	3 805(16)	2 515(51)	2 660(17)
C(1)	2 003(13)	4 644(18)	548(24)
C(2)	2 068(16)	4 718(20)	−578(25)
C(3)	1 724(12)	4 100(17)	−1 256(18)
C(16)	528(12)	848(16)	−875(18)
C(17)	473(14)	210(21)	−128(19)
C(18)	667(13)	380(19)	886(21)
C(31)	3 298(14)	2 516(68)	1 752(23)
C(32)	3 415(15)	3 199(27)	884(32)
C(33)	3 768(28)	3 389(21)	3 292(53)
C(34)	4 012(23)	3 435(41)	4 402(42)
C(35)	4 494(15)	2 389(15)	2 260(29)
C(36)	4 572(19)	1 506(38)	1 645(52)
C(37)	3 646(33)	1 634(51)	3 280(58)
C(38)	3 048(21)	1 409(40)	3 700(47)
C(4)	2 200(13)	5 427(18)	1 234(20)
C(5)	2 529(15)	6 186(21)	801(24)
C(6)	2 700(18)	6 922(26)	1 448(30)
C(7)	2 511(21)	6 885(29)	2 522(28)
C(8)	2 185(22)	6 182(32)	2 949(36)
C(9)	1 997(16)	5 413(23)	2 283(26)
C(10)	1 767(14)	4 234(19)	−2 460(17)
C(11)	1 242(19)	3 870(20)	−3 034(23)
C(12)	1 263(20)	3 980(22)	−4 156(24)
C(13)	1 737(17)	4 520(25)	−4 636(28)
C(14)	2 210(18)	4 927(28)	−4 030(30)
C(15)	2 260(19)	4 823(29)	−2 883(34)
C(19)	658(15)	−397(22)	1 673(26)
C(20)	388(17)	−1 285(26)	1 456(28)
C(21)	390(18)	−2 004(27)	2 216(31)
C(22)	714(20)	−1 809(29)	3 177(33)
C(23)	1 012(20)	−940(30)	3 400(33)
C(24)	956(16)	−205(25)	2 656(25)
C(25)	333(11)	630(16)	−2 044(18)
C(26)	688(16)	1 040(23)	−2 904(27)
C(27)	520(16)	793(24)	−3 991(28)
C(28)	44(17)	120(26)	−4 075(27)
C(29)	−277(16)	−230(23)	−3 288(28)
C(30)	−184(13)	−2(20)	−2 221(23)

All the calculations were performed using the '*X*-Ray '70' program system. Final atomic parameters are given in Table 2, bond lengths and angles in Tables 3 and 4. Structure factor tables and thermal parameters are available as Supplementary Publication No. SUP 22194 (14 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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DISCUSSION

Description of the Structure.—The complex can be formulated as $[NEt_4][UO_2(dppd)_2(NO_3)]$. As shown in Figure 1, the diketonate groups act as bidentate ligands, the fifth equatorial co-ordination site being occupied by the unidentate nitrate group. The resulting co-ordination polyhedron around the uranium atom is a quasi-regular pentagonal bipyramid. The best equatorial plane, which is inclined by 23° to the *bc* plane of the cell, can be described by the equation $20.65x - 6.60y - 1.53z = 0.75$ Å. The five equatorial oxygens are approximately planar and their deviations from the plane are: O(1) 0.03, O(2) 0.01, O(3) 0.10, O(4) −0.11, and O(5) −0.11 Å. The uranium atom is also slightly displaced (by 0.08 Å) from the plane.

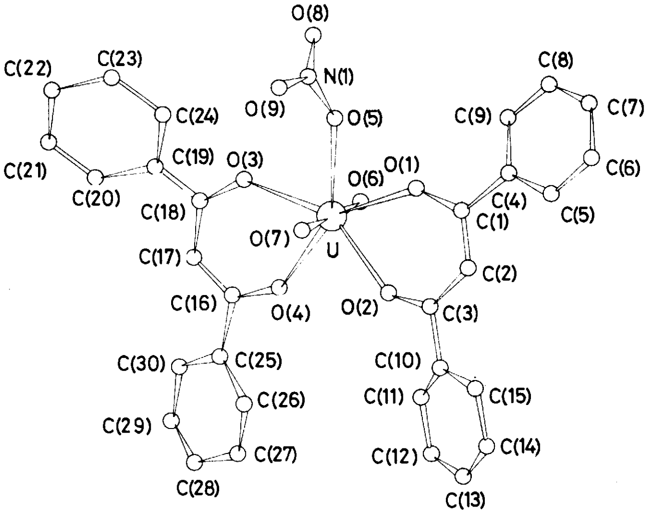

FIGURE 1 Numbering scheme for the $[UO_2(dppd)_2(NO_3)]^-$ anion

TABLE 3

Intramolecular bond lengths (Å) with estimated standard deviations

(*a*) Uranium core			
U–O(1)	2.41(2)	U–O(5)	2.46(4)
U–O(2)	2.37(2)	U–O(6)	1.77(2)
U–O(3)	2.31(2)	U–O(7)	1.75(2)
U–O(4)	2.32(2)		
(*b*) Ligands *			
O(1)–C(1)	1.28(4)	O(3)–C(18)	1.26(3)
O(2)–C(3)	1.26(3)	O(4)–C(16)	1.29(3)
C(1)–C(2)	1.43(4)	C(16)–C(17)	1.33(4)
C(2)–C(3)	1.43(4)	C(17)–C(18)	1.36(4)
C(1)–C(4)	1.48(4)	C(16)–C(25)	1.56(3)
C(3)–C(10)	1.54(3)	C(18)–C(19)	1.51(4)
(*c*) Nitrate			
N(1)–O(5)	1.18(5)	N(1)–O(9)	1.18(5)
N(1)–O(8)	1.20(6)		
(*d*) Cation			
N(2)–C(31)	1.54(4)	C(31)–C(32)	1.50(8)
N(2)–C(33)	1.50(8)	C(33)–C(34)	1.49(8)
N(2)–C(35)	1.61(5)	C(35)–C(36)	1.52(8)
N(2)–C(37)	1.54(9)	C(37)–C(38)	1.50(9)

* The carbon–carbon distances in the phenyl rings have normal values.

The uranyl group. The U–O bond lengths of the uranyl group [1.77(2) and 1.75(2) Å], which is approximately linear [175(1)°], are normal. $\nu_{asym}(UO_2)$ is observed at 900 cm^{-1}, very close to the values of neutral[3,8-10,21] and anionic[22] equatorially five-co-ordinate complexes, so that there is no unambiguous correlation between the uranyl asymmetric stretch and the strength of the ligand field. A weak band at 269 cm^{-1} can be tentatively assigned to the deformation frequency ν_2(O–U–O).

The nitrate group. The U–O(5) distance [2.43(2) Å] is significantly shorter than in uranyl complexes where the nitrate group is chelated, probably because of a different bonding mode. The high temperature factors of the nitrogen and of the peripheral oxygen atoms may indicate the presence of some disorder, or, more probably, free oscillation in a relatively large hole in the packing. Since in nitrato-complexes the D_{3h} symmetry of the free ion is lowered to C_{2v}, it is not possible to distinguish between the three possible bonding modes of nitrate ion (unidentate, bidentate, or bridging) by means of the selection rules alone. Moreover, the suggestion that the doubly degenerate asymmetric-stretching vibration of nitrate ion should split on co-ordination[23] owing to the reduced symmetry of the nitrate, and that the extent of the splitting can be used as a guide to the co-ordination mode,[24,25] is not always reliable. For example, the unidentate nitrate groups in $Cs_2[U(NO_3)_6]$ give almost

TABLE 4

Intramolecular bond angles (°) with estimated standard deviations

(*a*) Uranium core			
O(1)–U–O(2)	69(1)	O(1)–U–O(5)	69(1)
O(3)–U–O(4)	72(1)	O(3)–U–O(5)	75(1)
O(2)–U–O(4)	75(1)	O(6)–U–O(7)	175(1)
(*b*) Ligands *			
U–O(1)–C(1)	139(2)	U–O(3)–C(18)	135(2)
U–O(2)–C(3)	139(2)	U–O(4)–C(16)	134(2)
O(1)–C(1)–C(2)	124(3)	O(3)–C(18)–C(17)	127(3)
O(1)–C(1)–C(4)	117(3)	O(3)–C(18)–C(19)	114(2)
C(2)–C(1)–C(4)	119(2)	C(17)–C(18)–C(19)	119(3)
O(2)–C(3)–C(2)	126(2)	O(4)–C(16)–C(17)	128(2)
O(2)–C(3)–C(10)	115(2)	O(4)–C(16)–C(25)	111(2)
C(1)–C(2)–C(3)	120(2)	C(16)–C(17)–C(18)	121(3)
C(2)–C(1)–C(4)	119(2)	C(17)–C(18)–C(19)	119(3)
C(2)–C(3)–C(10)	119(2)	C(17)–C(16)–C(25)	120(2)
(*c*) Nitrate			
U–O(5)–N(1)	134(3)	O(5)–N(1)–O(9)	111(4)
O(5)–N(1)–O(8)	114(6)	O(8)–N(1)–O(9)	130(4)
(*d*) Cation			
C(31)–N(2)–C(33)	111(5)	N(2)–C(31)–C(32)	116(5)
C(31)–N(2)–C(35)	111(2)	N(2)–C(33)–C(34)	120(4)
C(31)–N(2)–C(37)	104(5)	N(2)–C(35)–C(36)	112(3)
C(33)–N(2)–C(35)	112(4)	N(2)–C(37)–C(38)	116(4)
C(33)–N(2)–C(37)	115(4)		
C(35)–N(2)–C(37)	103(4)		

* Bond angles in the phenyl rings have normal values.

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the same splitting as the bidentate nitrate groups in $Rb[UO_2(NO_3)_3]$. Splittings of the same magnitude have been recently reported for a series of uranyl complexes containing uni- or bi-dentate nitrate and also multidentate Schiff bases.[26] In the present case, where the nitrate group is unidentate, the stretching vibrations can be tentatively assigned at 1 449 and 1 290 cm^{-1}. (This region is rather complex because of the presence of bands of the diketone.) More useful in this context are the stretching bands in the far-i.r. region. The single i.r.-active band at 255 cm^{-1} for the present complex is in accordance with the suggestion that unidentate nitrate groups exhibit only one metal–oxygen frequency, whereas bidentate nitrate groups exhibit two.[27,28]

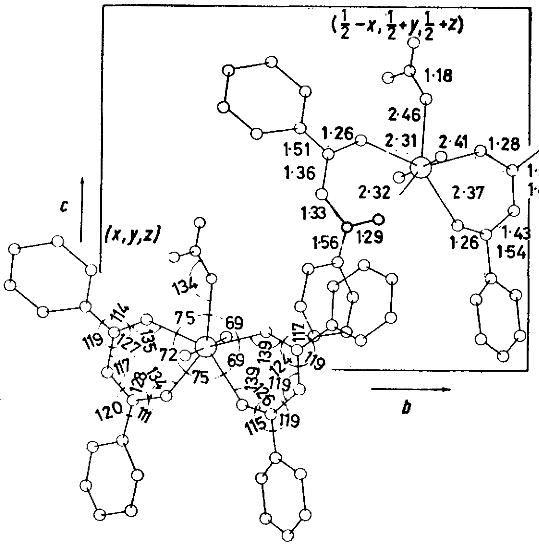

FIGURE 2 Projection of the structure on [100]. In order to avoid superimpositions, only the anions at positions x, y, z and $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ are shown and the cations are omitted

The diketonate ligand. The diketone ligands are chelated to uranium through the oxygen atoms, thus allowing the formation of two six-membered rings. As shown in Figure 2, where two units of the complex anion are shown, substitution of the ligand hydrogen atoms by the metal atom results in stabilization of the enolic form due to the presence of pseudo-aromatic systems characterized by delocalized single and double bonds. Most of the bond parameters are roughly comparable in the two organic moieties. In particular, the data suggest a symmetrical electron distribution in the chelate rings with local C_{2v} symmetry. However, the U–O(1) and U–O(2) distances (mean 2.39 Å) are significantly longer than U–O(3) and U–O(4) (2.31 and 2.32 Å). Accordingly the angles subtended at uranium are slightly different, as are the U–O–C angles (both 139° in the first, but 135 and 134° in the second, ligand). Co-ordination of the diketone to the uranium atom results in a lowering of the carbonyl-stretching frequency to 1 537 cm^{-1}, which appears as a single strong band typical of uranyl β-diketonates in which both the diketones are bidentate.[10] The assignments of the U–O(β-diketone) stretching frequencies are more difficult. Bands at 602, 518, 448, and 425 cm^{-1} are present which could be assigned to these vibrations. Since preliminary spectral measurements on the series $[UO_2(diketonate)_2X]^-$ (X = Cl, Br, I, SCN, $MeCO_2$, *etc.*) [22] show that only bands corresponding to those at 602 and 425 cm^{-1} are nearly always present, we favour the assignment of these bands to ν(U–O). The corresponding bands in the spectrum of bis(pentane-2,4-dionato)copper(II) at 615 and 455 cm^{-1} are reliably assigned [29] on the basis of normal-co-ordinate [30,31] and ^{18}O-labelling studies [32] to ν(Cu–O). That ν(U–O) is of lower frequency than ν(Cu–O) is expected in view of the greater mass and higher co-ordination number of the uranium atom. A contribution having the opposite sign to that expected, due to the partial negative charge on the uranium atom, is not effective, as supported by the ^1H n.m.r. spectrum. The resonances of both the phenyl and ring CH hydrogens lie at about the same frequencies as for neutral dppd complexes.[8]

The electronic spectrum of the complex in acetonitrile is very similar to that reported for $[UO_2(dppd)_2]$, even if some variations in the molar absorption coefficients can be observed. Bands at 278 and 337 nm correspond to those of the complexing diketone (253 and 342 nm in the free diketone). The third band at 397 nm due to the uranyl group is lacking in the spectrum of the dppd ligand and shows a continuous structureless shape quite different from the sharp narrow peaks in the 360—490 nm region due to the free uranyl group.

The cation. A projection of the tetraethylammonium cation on to (001) is shown in Figure 3. N–C Bond lengths are 1.50—1.61 Å. The ethyl group, and in particular the terminal carbon atoms, undergoes, as expected, large thermal vibrations which render the positions of the atoms less definite. This is also indicated by the relatively high standard deviations of these bonds.

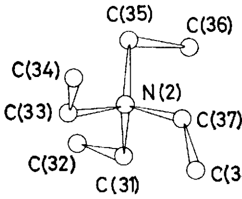

FIGURE 3 Numbering scheme for the $[NEt_4]^+$ cation

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