symmetry can be approximated virtually to C_{2h}. The reflectance spectrum of the *S*-peida dimer resembles that of the nta dimer in 9000–20 000-cm^{-1} region. This indicates that these complexes have similar electronic structures, although the dimers in the former and latter are regarded crystallographically as class II and class III ions, respectively. The absorption around 10 000 cm^{-1} is characteristic of the mixed-valence dimer. No such band is found in the uninuclear VO^{2+} and VO_2^+ complexes.

The linearity and bond length in V–O$_b$–V in these dimers indicate the presence of a multiple bonding. In the symmetric C_{2h} dimer, the bonding in V–O$_b$–V may be qualitatively described as follows. The p_y (O$_b$) orbital participates in σ bonding along with the $d_{x^2-y^2}$ orbitals of two vanadium atoms (the *y* axis parallels the V–O$_b$–V bond). Both the p_x and p_z orbitals of O$_b$ are capable of coupling with metal d_{xy} and d_{yz} to give π bonds, but the d_{xy}–p_x–d_{xy} set is energetically more favorable than the d_{yz}–p_z–d_{yz} set. The bonding orbital in the former set (a_u) accommodates two π electrons. The single d electron in this system may occupy the nonbonding b_g orbital mainly composed of the metal d_{xy} orbitals.

The orbital of the nonsymmetric dimer corresponding to the nonbonding orbital in the symmetric dimer mainly consists of the d_{xy} orbital of the V_A atom, since the d electron is virtually localized at the V_A center as described above. The polarized charge distribution around the dimer seems to cause the localization of the electron. The absorption at $\sim$10 000 cm^{-1} in the symmetric dimer may arise from an electronic excitation from the nonbonding to antibonding (a_u^*) orbital. The antibonding orbital of the nonsymmetric dimer must have a greater contribution from the d_{xy} orbital of V_B than that of V_A, and in this sense the lowest energy absorption in the solid state may be regarded as a kind of intervalence-transfer transition.

Registry No. **1**, 81898-97-7; **2**, 84863-66-1; **3**, 84894-05-3.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, hydrogen atom coordinates, and anisotropic thermal parameters (14 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Solvent-Extraction Complexes of the Uranyl Ion. 2. Crystal and Molecular Structures of *catena*-Bis(μ-di-*n*-butyl phosphato-*O*,*O*′)dioxouranium(VI) and Bis(μ-di-*n*-butyl phosphato-*O*,*O*′)bis[(nitrato)(tri-*n*-butylphosphine oxide)dioxouranium(VI)]

JOHN H. BURNS

Received September 16, 1982

Two complexes of the uranyl ion with organophosphorus extractants have been analyzed by single-crystal X-ray diffraction methods. A polymeric complex, $UO_2[(C_4H_9)_2PO_4]_2$, is formed with dibutylphosphoric acid; and with a mixture of this acid and tributylphosphine oxide a dimeric complex having the composition $\{UO_2[(C_4H_9)_2PO_4][(C_4H_9)_3PO]NO_3\}_2$ is formed. The first of these is triclinic, $P\bar{1}$, with a = 8.402 (6) Å, b = 15.648 (9) Å, c = 5.385 (3) Å, α = 99.46 (4)°, β = 98.51 (4)°, γ = 70.44 (3)°, and Z = 1; the second is also triclinic, $P\bar{1}$, with a = 13.510 (6) Å, b = 13.741 (6) Å, c = 10.055 (4) Å, α = 121.32 (2)°, β = 100.28 (3)°, γ = 80.00 (4)°, and Z = 1 (dimer). In each structure, pairs of linear uranyl ions are bridged by two dibutyl phosphate ions. In one case the bridging is repeated indefinitely to form a polymer, and each uranyl ion has four O atoms about its equator. The other structure is dimeric, and the chain is terminated by NO_3^- ions and phosphine oxide molecules at the equators of the uranyl ions.

Introduction

A variety of organophosphorus compounds when dissolved in organic solvents are effective in extracting U(VI) from acidic aqueous solutions.[1] In the liquid–liquid extraction process usually employed, the UO_2^{2+} ion moves from the aqueous phase to the organic as its aqueous solvation sphere is replaced by organophosphorus ligands to form extraction complexes. The structures of a number of these complexes are being studied in order better to understand the process of extraction. One such structure, previously reported,[2] is that of $UO_2(TBPO)_2(NO_3)_2$, in which TBPO ≡ tri-*n*-butylphosphine oxide. Here the equatorial plane of the UO_2^{2+} ion contains no water but is occupied by two molecules of TBPO and two NO_3^- ions. An analogous arrangement to this also exists in $UO_2L_2(NO_3)_2$ in cases where L = triethyl phosphate,[3] triisobutyl phosphate,[4] and triphenylphosphine oxide.[5]

There is also the interesting question of why certain combinations of reagents are better extractants than either of the components alone (the so-called synergistic effect[6–8]). Hence, in addition to the complex with TBPO mentioned above, a complex with di-*n*-butylphosphoric acid (HDBP) has been studied as well as a complex with a mixture of the two ligands. These latter two uranyl complexes are reported here. From these crystal structure analyses it can be seen how each component combines with the uranyl ion and what the result is of using a mixture of the two.

Experimental Section

Preparation of $UO_2(DBP)_2$. Di-*n*-butylphosphoric acid was obtained from a mixture of mono- and dibutylphosphoric acids (Mobil Chemical Co., Richmond, VA) by dissolving the mixture in benzene and extracting out the monoacid with water. A 1:2 mixture of $UO_2(NO_3)_2{\cdot}6H_2O$ and HDBP was heated to about 65 °C until it was liquid; in the process there were an evolution of brown oxides of nitrogen and the formation of tiny droplets of H_2O. The yellow liquid was desiccated over H_2SO_4 and gradually crystallized as a mass of thin plates of $UO_2(DBP)_2$. These bend easily or split into fibers, showing a mechanical property related to their polymeric structure.

Preparation of $UO_2(DBP)(TBPO)NO_3$. A 1:1:2 mixture of $UO_2(NO_3)_2{\cdot}6H_2O$, TBPO (Carlisle Chemical Works, Reading, OH),

---

[1] Blake, C. A., Jr.; Baes, C. F., Jr.; Brown, K. B. *Ind. Eng. Chem.* **1958**, *50*, 1763.

[2] Part 1: Burns, J. H. *Inorg. Chem.* **1981**, *20*, 3868.

[3] Fleming, J. E.; Lynton, H. *Chem. Ind.* (*London*) **1960**, 1415.

[4] Burns, J. H.; Brown, G. M., unpublished results.

[5] Alcock, N. W.; Roberts, M. M.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1982**, 25.

[6] Baes, C. F., Jr. *Nucl. Sci. Eng.* **1963**, *16*, 405.

[7] Deane, A. M.; Kennedy, J.; Sammes, P. G. *Chem. Ind.* (*London*) **1960**, 443.

[8] Dyrssen, D.; Kuca, L. *Acta Chem. Scand.* **1960**, *14*, 1945.

Table I. Crystal Data and Experimental Variables for X-ray Diffraction

	$UO_2(DBP)_2$	$[UO_2(DBP)(TBPO)NO_3]_2$
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.402 (6)	13.510 (6)
b, Å	15.648 (9)	13.741 (6)
c, Å	5.385 (3)	10.055 (4)
α, deg	99.46 (4)	121.32 (2)
β, deg	98.51 (4)	100.28 (3)
γ, deg	70.44 (3)	80.00 (4)
t, °C	25	23
Z	1	1 (dimer)
mol wt	688.4	1519.1
V(cell), Å^3	658.1	1562.4
ρ(calcd), g cm^{-3}	1.74	1.61
ρ(exptl), g cm^{-3}	1.73	1.55
μ, cm^{-1}	61.2	50.9
$F(000)$	334	748
reflcns measd	$h, \pm k, \pm l$	$h, \pm k, \pm l$
total reflcns	961	3141
$2\theta_{max}$, deg	37	41
reflcns > 3σ	732	1808
radiation	Mo Kα (Nb filter)	Mo Kα
bkgd time	$^1/_{10}$ peak time	$^1/_{10}$ peak time
scan range in 2θ, deg	2.12–2.36	1.24–1.96

and HDBP was heated to 70 °C to form a homogeneous yellow liquid. It remained liquid at room temperature, but cycling to ice temperature and desiccating over H_2SO_4 eventually induced crystallization. Thick, platelike crystals were separated from the excess HDBP for use in X-ray diffraction.

X-ray Diffraction. Precession photographs were taken of each of the compounds, revealing triclinic symmetry and no systematic absences. For determination of accurate unit-cell dimensions and for measurement of intensities, a computer-controlled Picker four-circle diffractometer and Mo Kα radiation were employed. The crystal of $UO_2(DBP)_2$ used for these measurements was a parallelepiped of dimensions 0.021 × 0.018 × 0.003 cm; for $UO_2(DBP)(TBPO)NO_3$ the data were collected in two parts by using two platelets of dimensions of 0.035 × 0.011 × 0.008 cm and 0.048 × 0.017 × 0.008 cm, respectively. Each sample was enclosed in a thin-walled glass capillary tube and mounted with its longest dimension approximately parallel to the ϕ axis. A standard reflection was measured hourly.

The crystal data and various experimental variables are given in Table I.

Structure Determinations and Refinements

Data Reduction. The observed intensities were corrected for Lorentz and polarization effects and normalized by applying factors obtained by interpolation between measurements of the standard reflections.[9] A correction for the effect of absorption was made by using measurements of the crystals' bounding planes to calculate transmission factors. These ranged from 0.37 to 0.83 for the $UO_2(DBP)_2$ data and from 0.58 to 0.71 and 0.43 to 0.67 for the data from the two crystals of $UO_2(DBP)(TBPO)NO_3$. After combination of replicate measurements, there resulted, for $UO_2(DBP)_2$, 732 observed structure-factor squares, F_o^2, larger than 3σ, and for $UO_2(DBP)(TBPO)NO_3$, 1808. The variances of these measurements, $\sigma^2(F_o^2)$, were taken to be equal to $\sigma_c^2 + (0.05F_o^2)^2$, in which σ_c^2 is attributed to counting statistics and the other term is an estimate of systematic errors. Relatively few reflections were measured in these substances because the intensities declined very rapidly with increasing Bragg angle.

Table II. Atomic Coordinates and Standard Deviations for $UO_2(DBP)_2$

atom	x	y	z
U	0	0	0
P	0.0548 (17)	0.1454 (8)	−0.4168 (18)
O(1)	0.095 (2)	0.081 (1)	−0.218 (3)
O(2)	−0.020 (3)	0.113 (1)	−0.666 (3)
O(3)	−0.081 (4)	0.238 (2)	−0.323 (4)
O(4)	0.211 (5)	0.174 (2)	−0.444 (4)
O(5)	−0.219 (3)	0.065 (1)	−0.120 (5)
C(1)	−0.072 (7)	0.290 (4)	−0.077 (7)
C(2)	−0.190 (8)	0.379 (4)	−0.045 (10)
C(3)	−0.147 (8)	0.427 (4)	0.221 (9)
C(4)	−0.272 (15)	0.509 (5)	0.233 (14)
C(5)	0.365 (6)	0.108 (3)	−0.495 (10)
C(6)	0.450 (8)	0.149 (5)	−0.653 (11)
C(7A)	0.412 (20)	0.236 (13)	−0.779 (33)
C(7B)	0.454 (11)	0.239 (7)	−0.557 (16)
C(8)	0.508 (7)	0.282 (4)	−0.751 (12)

Structure Determinations. Patterson maps were calculated for each structure and the U and P atomic sites readily found. The other non-hydrogen atoms were located in subsequent electron-density maps calculated by using the phases determined by the heavier atoms. Hydrogen atoms were not placed in either structure. Both structures were assumed to be centrosymmetric and were satisfactorily refined in space group $P\bar{1}$. In $UO_2(DBP)_2$ the U atom is at a center of symmetry, Wyckoff site 1(a), and all other atoms occupy 2(i) sites. The dimeric molecule $[UO_2(DBP)(TBPO)NO_3]_2$ is also centrosymmetric, but all its atoms occupy 2(i) sites. For both compounds the stoichiometry became known only as the structure was determined.

The butyl groups are quite flexible and undergo considerable thermal motion. For each structure the C atoms were difficult to find in the electron-density maps when they were away from the end where the group was attached to a P or O atom. The peaks for atom C(7) of the $UO_2(DBP)_2$ structure and atom C(16) of the $UO_2(DBP)(TBPO)NO_3$ structure were so elongated and/or split that a disordered description of these atoms seemed appropriate. Obviously, if one atom of a butyl chain is disordered, it is likely that those attached to it are also; but if this be the case, the "partial" atoms are not far enough apart to be resolved and could not be treated separately. Hence, only one C atom in each structure was treated as disordered.

Refinement of the $UO_2(DBP)_2$ Structure. The coordinates and anisotropic thermal parameters of 15 atoms were refined by the method of least squares (except the U atom was fixed at the origin and C(7A) and C(7B) were given isotropic thermal parameters). The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, wherein F_c is the calculated structure factor and the weights, w, are taken as $1/\sigma^2(F_o^2)$. Scattering factors of neutral atoms were used;[10] and for uranium anomalous dispersion corrections were included.[11] Atom C(7) was distributed 1:2 over sites C(7A) and C(7B). At convergence, the agreement index, $R = \sum||F_o| - |F_c||/\sum|F_o|$, was 0.069; the weighted index, R_w, was 0.146; and σ_1 was 2.02. This refinement used 732 observations greater than 3σ and 133 parameters.

Refinement of the $UO_2(DBP)(TBPO)NO_3$ Structure. The coordinates and anisotropic thermal parameters of all 34 non-hydrogen atoms of the asymmetric unit were refined by the method of least squares except for atom C(16), which was distributed equally over two sites and given isotropic thermal motion. The scattering factors and the quantity minimized were the same as above. At convergence the measures of agreement were as follows: $R = 0.052$, $R_w = 0.098$, $\sigma_1 = 1.28$. Reflections having $2\theta < 11°$ were omitted because of background problems, leaving some 1746 larger than 3σ for the refinement of 309 parameters.

Atomic coordinates are listed in Tables II and III for $UO_2(DBP)_2$ and $UO_2(DBP)(TBPO)NO_3$, respectively. Thermal parameters, U_{ij}, as well as lists of structure amplitudes for both structures are available as supplementary material.

Results and Discussion

Description of Structures. In crystals of $UO_2(DBP)_2$ the linear uranyl ions are doubly bridged at their equators by dibutyl phosphate (DBP) groups, which are bonded to the U atoms by their O atoms (Figure 1); this bridging produces continuous chains along the c axis of the crystal. Each U atom has only four O atoms around its equator. Extending out from

---

(9) The calculations in this work employed the following Oak Ridge computer programs: data reduction and absorption corrections with ORDATLIB (Ellison et al.); Fourier maps with ORFFP (Levy); least squares with ORXFLS-4 (Busing et al.); bond lengths and angles with ORFFE-4 (Busing et al.); drawings with ORTEP-II (Johnson).

(10) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

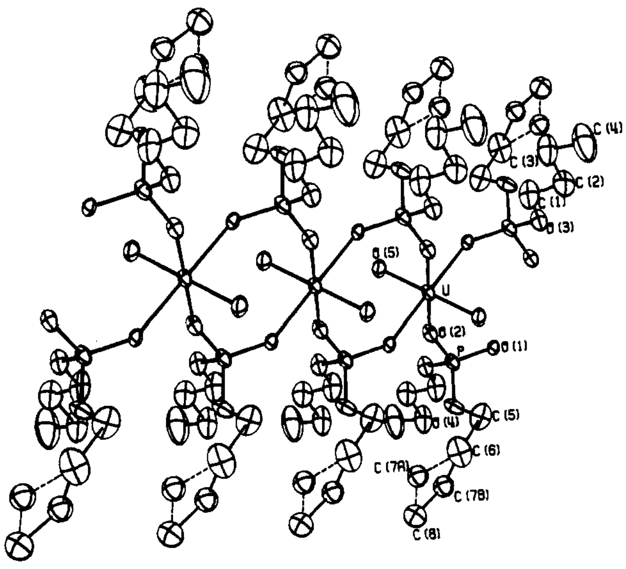

Figure 1. Portion of a polymeric chain of $UO_2(DBP)_2$ with atoms represented by their 20% probability ellipsoids. The numbering of atoms corresponds to that in Table II.

the chains are the *n*-butyl groups, which effectively enclose the uranyl ions and provide them a hydrophobic exterior. The butyl groups have large thermal motions and/or disorder. There is no cross-linking of chains except through weak van der Waals forces, and the manner in which the chains are packed in the crystal is shown in Figure 2. The polymeric nature of the structure is reflected in the mechanical properties of the crystals as already indicated, and they split very easily parallel to the *c* axis.

The structure of $UO_2(DBP)(TBPO)NO_3$ consists of dimeric molecules with uranyl ions doubly bridged in the same fashion as in $UO_2(DBP)_2$; but instead of the chain's continuing, it is terminated by a bidentate NO_3^- ion and a monodentate molecule of TBPO (Figure 3). The uranyl ions thus have five O atoms at their equators. Each centrosymmetric dimer contains five independent butyl groups; they are described as having large thermal motions and some disorder. Packing of molecules is shown in Figure 4.

Table III. Atomic Coordinates and Standard Deviations for $UO_2(DBP)(TBPO)NO_3$

atom	*x*	*y*	*z*
U	0.07386 (6)	0.20947 (7)	0.0554 (1)
P(1)	−0.1595 (6)	0.0721 (6)	−0.0335 (9)
P(2)	−0.1123 (5)	0.4593 (5)	0.1422 (7)
O(1)	0.0834 (10)	0.2774 (11)	0.2563 (16)
O(2)	0.0681 (10)	0.1471 (11)	−0.1452 (17)
O(3)	−0.0770 (9)	0.1495 (10)	0.0421 (17)
O(4)	0.1337 (10)	0.0387 (10)	0.0385 (18)
O(5)	−0.0299 (9)	0.3638 (10)	0.0645 (15)
O(6)	0.2598 (12)	0.1930 (15)	0.0641 (18)
O(7)	0.1821 (15)	0.3473 (13)	0.0750 (18)
O(8)	0.3423 (17)	0.3175 (18)	0.0642 (26)
O(9)	−0.1951 (16)	0.0537 (18)	−0.1986 (33)
O(10)	−0.2563 (14)	0.1399 (13)	0.0523 (23)
N	0.265 (2)	0.286 (3)	0.070 (3)
C(1)	−0.144 (3)	−0.019 (3)	−0.327 (6)
C(2)	−0.218 (5)	−0.034 (5)	−0.476 (8)
C(3)	−0.303 (6)	−0.099 (6)	−0.507 (7)
C(4)	−0.365 (5)	−0.146 (6)	−0.655 (7)
C(5)	−0.350 (3)	0.085 (3)	−0.009 (4)
C(6)	−0.427 (3)	0.165 (5)	0.121 (10)
C(7)	−0.388 (5)	0.145 (7)	0.254 (10)
C(8)	−0.477 (6)	0.150 (8)	0.327 (9)
C(9)	−0.069 (2)	0.597 (1)	0.216 (2)
C(10)	0.016 (2)	0.619 (2)	0.351 (3)
C(11)	0.052 (2)	0.746 (3)	0.408 (3)
C(12)	0.125 (3)	0.787 (3)	0.549 (4)
C(13)	−0.155 (2)	0.448 (2)	0.290 (2)
C(14)	−0.239 (2)	0.544 (3)	0.371 (3)
C(15)	−0.277 (2)	0.525 (3)	0.498 (4)
C(16A)	−0.358 (7)	0.605 (7)	0.568 (9)
C(16B)	−0.360 (7)	0.477 (7)	0.454 (9)
C(17)	−0.218 (2)	0.459 (2)	0.002 (2)
C(18)	−0.265 (2)	0.342 (2)	−0.077 (4)
C(19)	−0.350 (4)	0.341 (4)	−0.213 (6)
C(20)	−0.435 (5)	0.383 (7)	−0.177 (7)

Although equatorial fourfold coordination of uranyl ions by O atoms is not common, there are several examples among phosphate minerals. Bridging of uranyl ions by phosphate (and arsenate) ions is present in $HUO_2PO_4{\cdot}4H_2O$[12] and a number

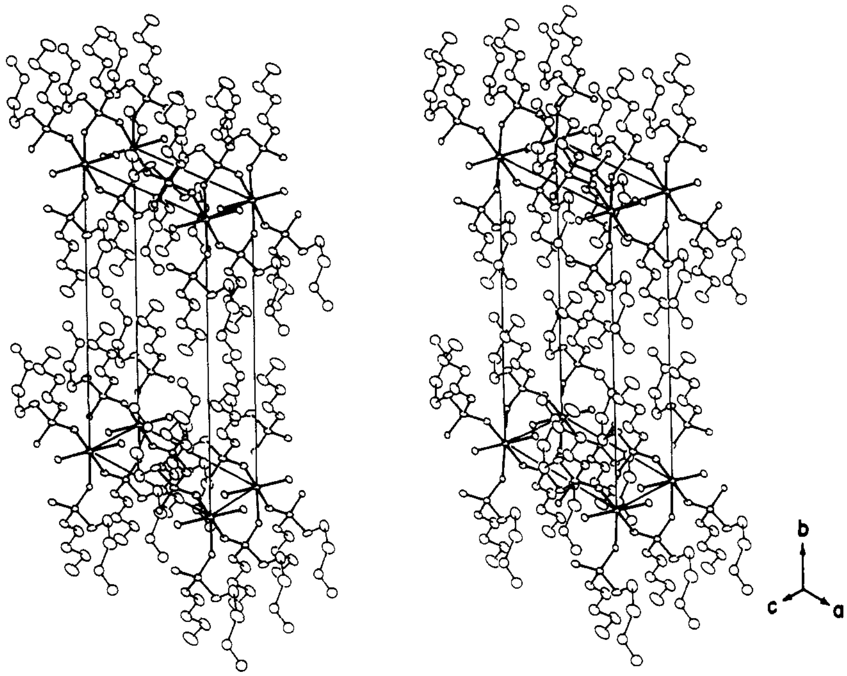

Figure 2. Stereoscopic drawing of a portion of the $UO_2(DBP)_2$ structure showing the packing of chains. (The disordered atom is shown at only one of its two sites.)

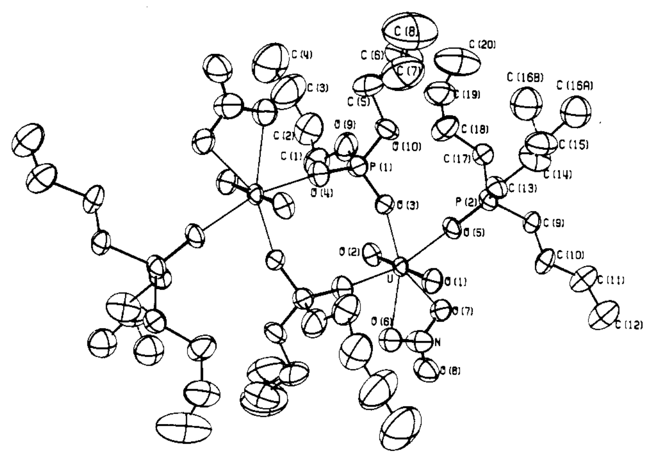

Figure 3. One molecule of $[UO_2(DBP)(TBPO)NO_3]_2$ with atoms represented by their 20% probability ellipsoids. The numbering of atoms corresponds to that in Table III.

Table IV. Interatomic Distances and Bond Angles with Standard Deviations for $UO_2(DBP)_2$

atoms	dist, Å	atoms	angle, deg
U-O(5)	1.86 (2)	U-O(1)-P	148 (1)
U-O(1)	2.25 (2)	U-O(2)-P	148 (1)
U-O(2)	2.29 (2)	O(1)-U-O(2)	91.5 (6)
P-O(1)	1.51 (2)	O(5)-U-O(1)	92.0 (9)
P-O(2)	1.48 (2)	O(5)-U-O(2)	92.0 (9)
P-O(3)	1.57 (3)	O(1)-P-O(2)	115 (1)
P-O(4)	1.55 (3)	O(1)-P-O(3)	109 (1)
O(3)-C(1)	1.44 (4)	O(1)-P-O(4)	111 (1)
C(1)-C(2)	1.41 (5)	O(2)-P-O(3)	105 (1)
C(2)-C(3)	1.56 (6)	O(2)-P-O(4)	111 (1)
C(3)-C(4)	1.36 (8)	O(3)-P-O(4)	104 (2)
O(4)-C(5)	1.39 (4)	P-O(3)-C(1)	126 (3)
C(5)-C(6)	1.52 (7)	O(3)-C(1)-C(2)	117 (4)
C(6)-C(7A)	1.53 (19)	C(1)-C(2)-C(3)	109 (5)
C(6)-C(7B)	1.43 (9)	C(2)-C(3)-C(4)	103 (6)
C(7A)-C(8)	1.23 (18)	P-O(4)-C(5)	121 (3)
C(7B)-C(8)	1.52 (9)	O(4)-C(5)-C(6)	107 (4)
		C(5)-C(6)-C(7A)	139 (8)
		C(5)-C(6)-C(7B)	115 (6)
		C(6)-C(7A)-C(8)	123 (13)
		C(6)-C(7B)-C(8)	111 (7)

of minerals of the torbernite group, including autunite[13] $[Ca(UO_2PO_4)_2 \cdot nH_2O, n \sim 10.5]$, metatorbernite[14] $[Cu(UO_2PO_4)_2 \cdot 8H_2O]$, and abernathyite[15] $[KUO_2AsO_4 \cdot 3H_2O]$. In these structures the inorganic PO_4^{3-} (and AsO_4^{3-}) ions bridge in two directions, involving all the O atoms, and there result uranyl-phosphate (arsenate) sheets instead of chains. Closely related to the present structures are the chains of uranyl ions found bridged by tetrahedral SO_4^{2-} ions in $UO_2SO_4 \cdot H_2SO_4 \cdot 5H_2O$,[16] $(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$,[17] and $K_2UO_2(SO_4)_2 \cdot 2H_2O$.[18] In each of these structures the uranyl equatorial coordination number is 5 and includes a water molecule.

The large thermal motions of the butyl groups in the present structures may be attributed to the flexibility of these carbon chains and the absence of significant restraining forces from neighbors as, for example, those of close-packed parallel chains in hydrocarbon structures.[19] In butane the anti and gauche conformations are not very different in energy;[20] both forms appear in the gas,[21] and in solids butyl groups adopt both forms and some intermediate between them.

Table V. Interatomic Distances and Bond Angles with Standard Deviations for $UO_2(DBP)(TBPO)NO_3$

atoms	dist, Å	atoms	angle, deg
U-O(1)	1.720 (13)	O(1)-U-O(2)	176.8 (6)
U-O(2)	1.726 (14)		
U-O(3)	2.29 (1)	U-O(3)-P(1)	154.9 (9)
U-O(4)	2.27 (1)	U-O(4)-P(1)	172.4 (9)
U-O(5)	2.30 (1)	U-O(5)-P(2)	148.4 (7)
U-O(6)	2.47 (2)	O(3)-P(1)-O(4)	114.4 (8)
U-O(7)	2.50 (1)	O(3)-P(1)-O(9)	110.1 (10)
P(1)-O(3)	1.49 (1)	O(3)-P(1)-O(10)	107.7 (10)
P(1)-O(4)	1.48 (1)	O(4)-P(1)-O(9)	110.8 (10)
P(1)-O(9)	1.54 (2)	O(4)-P(1)-O(10)	112.2 (9)
P(1)-O(10)	1.57 (2)	O(9)-P(1)-O(10)	100.8 (13)
P(2)-O(5)	1.52 (1)	O(5)-P(2)-C(9)	110.7 (8)
O(9)-C(1)	1.37 (3)	O(5)-P(2)-C(13)	110.2 (9)
O(10)-C(5)	1.45 (3)	O(5)-P(2)-C(17)	112.1 (9)
P(2)-C(9)	1.80 (2)	C(9)-P(2)-C(13)	112.4 (9)
P(2)-C(13)	1.77 (2)	C(9)-P(2)-C(17)	101.0 (10)
P(2)-C(17)	1.82 (2)	C(13)-P(2)-C(17)	110.2 (10)
N-O(6)	1.27 (2)	O(6)-N-O(7)	117 (3)
N-O(7)	1.27 (3)	O(6)-N-O(8)	124 (3)
N-O(8)	1.22 (2)	O(7)-N-O(8)	119 (3)
C(1)-C(2)	1.58 (6)	C(1)-C(2)-C(3)	113 (5)
C(2)-C(3)	1.46 (6)	C(2)-C(3)-C(4)	122 (6)
C(3)-C(4)	1.45 (6)	C(5)-C(6)-C(7)	104 (5)
C(5)-C(6)	1.61 (6)	C(6)-C(7)-C(8)	107 (7)
C(6)-C(7)	1.50 (7)	C(9)-C(10)-C(11)	106 (2)
C(7)-C(8)	1.50 (8)	C(10)-C(11)-C(12)	113 (3)
C(9)-C(10)	1.55 (3)	C(13)-C(14)-C(15)	109 (3)
C(10)-C(11)	1.65 (3)	C(14)-C(15)-C(16A)	111 (4)
C(11)-C(12)	1.47 (3)	C(14)-C(15)-C(16B)	116 (4)
C(13)-C(14)	1.54 (3)	C(17)-C(18)-C(19)	106 (2)
C(14)-C(15)	1.61 (3)	C(18)-C(19)-C(20)	117 (6)
C(15)-C(16A)	1.39 (8)		
C(15)-C(16A)	1.29 (8)		
C(17)-C(18)	1.58 (3)		
C(18)-C(19)	1.62 (5)		
C(19)-C(20)	1.21 (5)		

Bond lengths and angles for $UO_2(DBP)_2$ and $UO_2(DBP)(TBPO)NO_3$ are listed in Tables IV and V. It is of interest to compare the U=O distances in these two compounds and in $UO_2(TBPO)_2(NO_3)_2$. They are 1.858 (3), 1.72 (2), and 1.742 (7) Å, respectively. Because the length of this bond is affected by the number and strength of equatorial bonds (the more and stronger they are, the weaker the U=O bond[22]), it is curious that the longest uranyl ion only has fourfold equatorial coordination. Apparently these four phosphato O atoms have more electron-withdrawing ability than the combination of phosphoryl and nitrato O atoms in each of the other two compounds. In none of these structures is there any significant *inter*molecular interaction with the uranyl O atoms.

In $UO_2(DBP)(TBPO)NO_3$ the five equatorial O atoms can be fitted by a plane from which the largest deviation is 0.015 Å. The uranyl ion appears slightly bent, the O=U=O angle being 176.8 (7)°. Because of centrosymmetry the $UO_2(DBP)_2$

---

(12) Morosin, B. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3732.
(13) Bientema, J. *Recl. Trav. Chim. Pays-Bas* **1938**, *57*, 155.
(14) Ross, M.; Evans, H. T., Jr.; Appleman, D. E. *Am. Mineral.* **1964**, *49*, 1603.
(15) Ross, M.; Evans, H. T., Jr. *Am. Mineral.* **1964**, *49*, 1578.
(16) Alcock, N. W.; Roberts, M. M.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1982**, 869.
(17) Niinistö, L.; Toivonen, J.; Valkonen, J. *Acta Chem. Scand. Ser. A* **1978**, *A32*, 647.
(18) Niinistö, L.; Toivonen, J.; Valkonen, J. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 621.
(19) Müller, A. *Proc. R. Soc. London, Ser. A* **1928**, *120*, 437.
(20) Kitaigorodsky, A. I. "Molecular Crystals and Molecules"; Academic Press: New York, 1973; p 398.
(21) Bartell, L. S.; Kohl, D. *J. Chem. Phys.* **1963**, *39*, 3097.
(22) Zachariasen, W. H.; Plettinger, H. A. *Acta Crystallogr.* **1959**, *12*, 526. Zachariasen, W. H. in "Heavy Element Properties"; Müller, W., Blank, H., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; p 91. Burns, J. H.; Musikas, C. *Inorg. Chem.* **1977**, *16*, 1619.

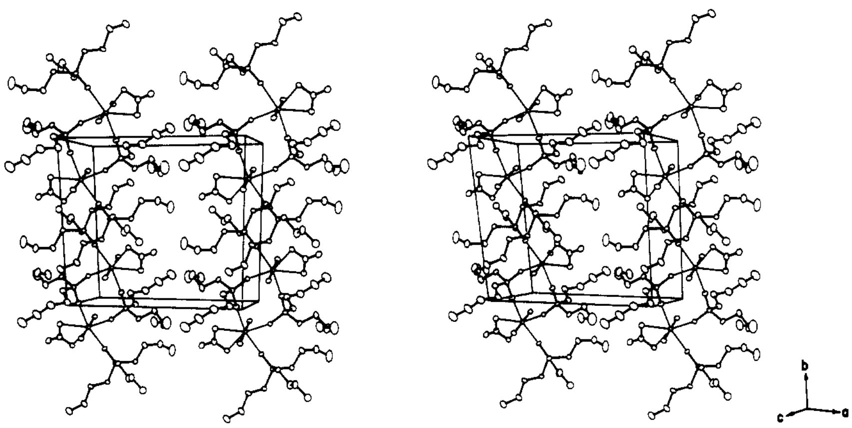

Figure 4. Stereoscopic drawing of a portion of the $UO_2(DBP)(TBPO)NO_3$ structure showing the packing of molecules. (The disordered atom is shown at only one of its two sites.)

structure has a linear UO_2 group and the equatorial atoms are exactly coplanar.

The dibutyl phosphato ions are of quite similar dimensions in the two compounds reported here. The P–O bonds to unsubstituted O atoms are shorter (~1.50 Å) than those to the other two O atoms (1.56 Å). The PO_4 group is an irregular tetrahedron with O–P–O angles deviating from tetrahedral by as much as 8°. The C atoms are not precisely determined in either structure because of their large thermal motion and the relatively small ratio of data to parameters. However, there is not much of chemical interest to be learned from the configurations of the butyl groups; and their exact positions do not seem to have much effect on the refinement of the rest of the structure. In $UO_2(DBP)_2$ the C–C bond lengths averaged 1.45 Å and, when corrected for thermal motion by using the riding model,[23] averaged 1.51 Å. The C–C–C bond angles averaged 115°, with an average deviation of ±9°. The corresponding averaged values in $UO_2(DBP)(TBPO)NO_3$ are 1.55 Å for temperature-corrected bond lengths and 111 ± 5° for bond angles. The lengths and angles in gaseous butane are 1.54 Å and 112.6°, respectively. Conformation angles[24] of butyl groups in $UO_2(DBP)_2$ are 178 (7)° for the ordered one and 129 (14) and −165 (5)° for the disordered one; the five butyl groups in $UO_2(DBP)(TBPO)NO_3$ have conformation angles of −165 (5), 145 (5), 174 (3), 176 (5), and 100 (5)° (disordered), and 89 (7)°. The geometries of the NO_3^- ion and the TBPO molecule in the dimer are quite similar to those in $UO_2(TBPO)_2(NO_3)_2$.

Significance for Solvent Extraction. The existence of a polymeric structure for the extraction complex $UO_2(DBP)_2$ was proposed by Healy and Kennedy,[25] who built on an earlier model used by Baes et al.[26] to explain the extraction of U(VI) from aqueous solutions by bis(2-ethylhexyl)phosphoric acid in hexane. The latter authors proposed that, in solutions of low U(VI) concentration, the uranyl ion would be complexed with four acid phosphate groups surrounding it equatorially, two of which would be protonated. Then, as the U(VI) concentration is increased, polymerization occurs through double bridging by phosphate groups; and the protons would be exchanged, except at the ends of the polymers. As evidence of such polymerization they found that, as the ratio of U to acid phosphate approached 1:2, the (organic) solutions containing the complex rapidly became very viscous. Although the polymers of $UO_2(DBP)_2$ in the crystal are effectively infinite in length, it is possible that, where they do terminate, the PO_4 group may have a proton attached (obviously beyond the range of X-ray detection).

When the neutral compound TBPO is added to a solution of HDBP, the extraction of UO_2^{2+} by the mixture is considerably increased beyond that of either component alone. This synergism is found in many systems composed of acidic and neutral organophosphorus compounds, and there is much written about the mechanism of this effect.[6-8] Elucidation of the structure of $UO_2(DBP)(TBPO)NO_3$ provides some new information for use in devising a satisfactory explanation. Of course the molecule found in the crystal may be different from the extraction complex in solution, but it at least represents one of the possibilities. Of interest then is its stoichiometry, which differs from that suggested previously and answers the question of substitution vs. addition by the neutral molecule in favor of the latter. Also, the nature of the bonding by this molecule is clarified as being a direct attachment to the U atom; the suggested[6] secondary attachment through hydrogen bonding is not found. Finally, since the dimer found in the mixed system appears to be a segment of the polymer found in $UO_2(DBP)_2$ that has been terminated by the neutral additive, it is suggestive that the synergism may be related to prevention of polymer formation. The confirmation of these speculations must await further studies, particularly those that will relate these findings in crystals to the situation existing in solution.

Acknowledgment. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp. I thank W. D. Arnold, Jr., for preparation of the HDBP and C. F. Baes, Jr., for helpful discussions.

Registry No. $UO_2(DBP)_2$, 33881-92-4; $[UO_2(DBP)(TBPO)NO_3]_2$, 84943-96-4.

Supplementary Material Available: A listing of observed and calculated structure amplitudes for both structures and two tables of thermal parameters (13 pages). Ordering information is given on any current masthead page.

---

(23) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1964**, *17*, 142.
(24) Klyne, W.; Prelog, V. *Experientia* **1960**, *16*, 521.
(25) Healy, T. V.; Kennedy, J. *J. Inorg. Nucl. Chem.* **1959**, *10*, 128.
(26) Baes, C. F., Jr.; Zingaro, R. A.; Coleman, C. F. *J. Phys. Chem.* **1958**, *62*, 129.