within the range observed in heterocyclic molecules (Abrahams, 1956). The S–O bond length of 1·491 Å agrees well with the values observed in other sulfoxides such as cycloalliin (Palmer & Lee, 1966).

The molecular packing is illustrated in Fig. 3. In retrospect we attribute our initial difficulty in solving the structure to the presence of an approximate glide along **c**, having a translation of 0·23*c* and relating molecule *A* to molecule *B*. All contacts to 4 Å were computed; the closest non-hydrogen contacts are O(1)*A*–C(4)*B*, 3·12 Å and O(1)*A*–C(5)*B*, 3·17 Å.

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1,4,7,10-Tetraoxacyclododecane–Uranyl Nitrate Dihydrate

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Abstract. $C_8H_{16}O_4UO_2(NO_3)_2.2H_2O$, monoclinic, $P2_1/c$, $a = 9{\cdot}048\ (5)$, $b = 14{\cdot}366\ (8)$, $c = 6{\cdot}720\ (26)$ Å, $\beta = 99{\cdot}38\ (15)°$, $M_r = 606{\cdot}26$, $Z = 2$, $D_o = 2{\cdot}327$, $D_x = 2{\cdot}236$ g cm^{-3}. The molecule has a crystallographic centre of symmetry which is occupied by the U atom. The uranyl group is surrounded equatorially by a near-planar hexagon comprised of four O atoms from the ether ring and two water O atoms. Intermolecular binding is a result of the hydrogen bonds between nitrate O atoms and the water molecules.

Introduction. This work is one of the first structural studies of 12-crown-4 ether and its complexes. The crystals used were supplied by the Chemistry Department of the University of Ankara.

The crystals were transparent, prismatic and determined to be twins with (100) composition plane. They were cut into single crystals having (010) as prominent faces. It was observed that the crystals decompose on exposure to X-rays. Thus three-dimensional data were collected with various crystals whose details are given in Table 1.

Systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ confirmed the space group as $P2_1/c$. 46 high-angle reflexions of $hk0$ and $h0l$, including 18 α_1,α_2 separated reflexions measured from the equi-inclination Weissenberg films, were used for the refinement of the lattice parameters with the least-squares computer program *CELCIUS* (Tegenfeldt, 1967). Ambiguity in the molecular formula was clarified by determining the number of water molecules. Intensity data were recorded with Cu $K\alpha$ radiation and the multiple-film technique. Intensities were measured with a Joyce–Loebl microdensitometer. Owing to the high linear absorption coefficient, $\mu = 374{\cdot}17$ cm^{-1} for Cu $K\alpha$ radiation, absorption corrections were made by the computer program *ABSOT* (Coppens, Leiserowitz & Rabinovich, 1967). 850 unique reflexions were obtained from the 2681 measured reflexions with $0 \le l \le 5$ and $0 \le k \le 1$. The *c* axis data were then brought to the same scale by means of the *b* axis data. Lorentz–polarization corrections were applied to the data in the usual way (Zalkin, 1967).

In the solution of the structure the heavy-atom method was employed. The distribution of the molecules among the equi-points showed that the asymmetric unit consists of one-half of the molecule, and that the U atoms occupy the special positions 2(*a*).

Table 1. *Description of the crystals used in the data collection*

(hkl) and D denote respectively the boundary planes and their distances from the arbitrary origins in the crystals. (HKL) represents the reciprocal layers for which data were collected for the corresponding crystals.

Crystal 1		Crystal 2		Crystal 3	
(HK0; HK1)		(HK2)		(HK3)	
(hkl)	D (mm)	(hkl)	D (mm)	(hkl)	D (mm)
(100)	0·11	(100)	0·05	(100)	0·18
($\bar{1}$00)	0·11	($\bar{1}$00)	0·05	($\bar{1}$00)	0·18
(010)	0·10	(010)	0·04	(010)	0·12
(0$\bar{1}$0)	0·10	(0$\bar{1}$0)	0·04	(0$\bar{1}$0)	0·12
(001)	0·16	($\bar{3}$04)	0·08	(00$\bar{1}$)	0·18
(00$\bar{1}$)	0·12	(00$\bar{1}$)	0·08	(304)	0·15
(30$\bar{1}$)	0·12			($\bar{3}$02)	0·19
($\bar{2}$01)	0·15				

Crystal 4		Crystal 5		Crystal 6	
(HK4)		(HK5)		(H0L; H1L)	
(hkl)	D (mm)	(hkl)	D (mm)	(hkl)	D (mm)
(100)	0·05	(100)	0·13	(100)	0·09
($\bar{1}$00)	0·05	($\bar{1}$00)	0·13	($\bar{1}$00)	0·09
(010)	0·04	(010)	0·10	(010)	0·09
(0$\bar{1}$0)	0·04	(0$\bar{1}$0)	0·10	(0$\bar{1}$0)	0·09
(001)	0·11	(001)	0·17	(001)	0·12
(00$\bar{1}$)	0·09	(00$\bar{1}$)	0·17	(01$\bar{1}$)	0·11
($\bar{3}$04)	0·11	($\bar{2}$01)	0·15		

Table 2. *Fractional coordinates and isotropic thermal parameters with standard deviations in parentheses*

	x	y	z	B (Å^2)
U	0·000 (0)	0·000 (0)	0·000 (0)	2·27 (4)
O(1)	0·000 (4)	0·000 (2)	0·245 (6)	2·06 (75)
O(2)	−0·265 (9)	0·000 (9)	−0·045 (12)	7·9 (1·1)
O(3)	−0·110 (13)	0·084 (7)	−0·150 (19)	11·7 (2·7)
O(4)	0·107 (10)	0·104 (5)	−0·129 (13)	8·9 (1·8)
O(5)	0·437 (9)	−0·125 (5)	0·330 (12)	7·5 (1·7)
O(6)	−0·441 (5)	−0·122 (3)	−0·379 (8)	4·0 (0·8)
O(7)	0·285 (7)	−0·120 (3)	0·572 (9)	6·0 (1·1)
C(1)	−0·099 (8)	0·165 (5)	−0·052 (12)	5·3 (1·3)
C(2)	0·060 (6)	0·203 (3)	−0·034 (10)	3·8 (0·9)
C(3)	0·202 (5)	0·019 (3)	−0·097 (9)	3·6 (0·9)
C(4)	0·118 (5)	−0·060 (3)	−0·015 (9)	3·3 (0·8)
N	0·406 (8)	−0·176 (5)	0·495 (12)	6·2 (1·3)

The position of the U atom was readily confirmed by the three-dimensional sharpened Patterson synthesis calculated by the computer program *DRF* (Zalkin, 1967). The reflexions of the type $k + l = 2n + 1$, constituting 1·8% of the entire data, appeared to be very weak when compared with the reflexions of $k + l = 2n$. This accounted for the twofold pseudosymmetry in the Fourier maps. Furthermore, the dominant scattering power of the U atom was the main reason for the inapplicability of the successive Fourier method to the structure. The uranium–light atom peaks of the three-dimensional sharpened Patterson map based on the c axis data were selected with the aid of the (010) sharpened Patterson projection of the b axis data. All the light atoms, except the H atoms, were thus found. The refinement was carried out with the full-matrix least-squares computer program *LALS* (Zalkin, 1968). The function minimized was $\Sigma\, w_{hkl}(|F_o| - |F_c|)^2$, where $w_{hkl} = 1/(\sigma F_o)^2$; σF_o denotes the standard deviation of the observed structure factor determined from the symmetry-related reflexions. The refinement of the positional and isotropic thermal parameters yielded the final $R = 0{\cdot}102$ ($R = \Sigma||F_o| - |F_c||/\Sigma\,|F_o|$) and $R_w = 0{\cdot}120$ $\{R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}\}$ for 736 reflexions.* For all 791 reflexions (including the very weak) $R = 0{\cdot}128$. The final positional and thermal parameters are listed in Table 2. In order to include the anomalous-dispersion effect in the calculation of the structure factors, the structure (which has a centre of symmetry) was treated as being noncentrosymmetric.

The scattering factors of all the atoms used were the neutral ones taken from the data of Cromer & Waber (1965); those of U^{2+} were derived by interpolation from U^0 and U^{3+}. The scattering factors were corrected for the effects of anomalous dispersion (Cromer, 1965).

Discussion. The (001) projection of the structure is shown in Fig. 1. Bond distances, angles and inter-

Table 3. *Distances* (Å) *and angles* (°) *with standard deviations in parentheses*

(i) denotes atoms generated by the symmetry centre.

Bond distances and angles

U–O(1)	1·65 (4)	O(2)–U–O(3)	58 (5)
U–O(2)	2·37 (8)	O(2^i)–U–O(4)	61 (4)
U–O(3)	1·77 (12)	O(3)–U–O(4)	61 (4)
U–O(4)	2·05 (8)	O(5)–N–O(6)	84 (6)
N–O(5)	1·40 (14)	O(5)–N–O(7)	104 (6)
N–O(6)	1·69 (12)	O(6)–N–O(7)	100 (5)
N–O(7)	1·52 (12)	O(3)–C(1)–C(2)	110 (6)
C(1)–O(3)	1·34 (13)	O(3^i)–C(4)–C(3)	132 (8)
C(1)–C(2)	1·53 (9)	O(4)–C(2)–C(1)	87 (5)
C(2)–O(4)	1·65 (10)	O(4)–C(3)–C(4)	110 (5)
C(3)–O(4)	1·49 (9)	C(1)–O(3)–C(4^i)	78 (8)
C(3)–C(4)	1·52 (6)	C(2)–O(4)–C(3)	146 (8)
C(4)–O(3^i)	1·18 (14)		

Interatomic distances and corresponding angles

O(2)–O(3)	2·06 (15)	O(2)–O(3)–O(4)	142 (8)
O(2^i)–O(4)	2·26 (14)	O(2^i)–O(4)–O(3)	119 (5)
O(2)–O(5^i)	2·89 (15)	O(3)–O(2)–O(4^i)	99 (6)
O(2)–O(6)	3·08 (12)	O(5)–O(6)–O(7)	60 (3)
O(2)–O(7)	3·65 (12)	O(5)–O(7)–O(6)	52 (3)
O(3)–O(4)	1·96 (15)	O(6)–O(5)–O(7)	68 (3)
O(5)–O(6)	2·08 (12)		
O(5)–O(7)	2·29 (13)		
O(6)–O(7)	2·45 (10)		

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32542 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

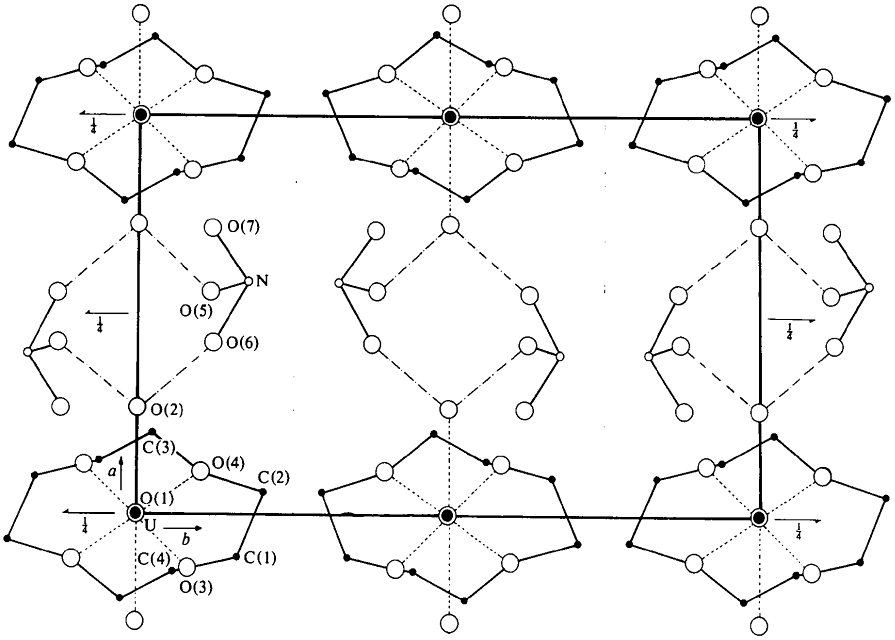

Fig. 1. The crystal structure viewed along **c**. Possible hydrogen bonds and covalent bonds are drawn as dotted–broken lines and full lines respectively. U coordination is represented by broken lines.

atomic distances and corresponding angles with their standard deviations are given in Table 3.

The complex is of the form 1:1. The U atom surrounded by the crown ether is located at the centre of symmetry. The U atom lies in the hole in the ether ring. The accommodation of the U atom in the 12-crown-4 ether confirms the estimated hole size of this type of crown ether (Pedersen, 1967; Frensdorff, 1971). The U atom, held by ion–dipole interaction between the uranyl cation and the crown ether ring, is also coordinated with the water molecules (Taylor & Mueller, 1965; Dalley, Mueller & Simonsen, 1971). As can be seen from Table 3, the crown ether and the water O atoms form a fairly regular planar hexagon whose normal makes an angle of 23 (4)° with the U–O(1) [1·65 (4) Å] bond which is parallel to the *c* axis. The O atoms coordinated to the U atom form a distorted hexagonal bipyramid.

Despite their rather large standard deviations, the C–C and C–O bonds of the ether ring lie in the range of expected average values (Davies & Hassel, 1963). The angles subtended at the C and O atoms in the ring seem to agree with those reported by Dunitz & Seiler (1974*a*,*b*).

It may be proposed that O(3)–C(1)–C(2)–O(4) and O(4)–C(3)–C(4)–O(3) subunits conform with the geometry of *ac*,*sp*,*ac* and *ac*,*ac*,*ac* respectively. The O atoms of the nitrate anion lie at the corners of an almost equilateral triangle having sides of 2·08 (12), 2·29 (13) and 2·45 (10) Å.

It is reasonable to consider that the distances O(2)–O(5$^{\mathrm{i}}$) = 2·89 (15) and O(2)–O(6) = 3·08 (12) Å are suitable for hydrogen bonding. It may thus be proposed that the NO_3 anions almost parallel to (010) link the molecules to form the chains extending along [101]. The decomposition of the crystals exposed to X-rays is an indication of the existence of the weak hydrogen bonds and van der Waals interactions in the crystal structure.

The large standard deviations obtained for the bond lengths and angles can be attributed to the presence of the heavy U atom at the special position and its scattering domination over the other light atoms (Stout & Jensen, 1968). Therefore a neutron diffraction study would be very valuable to fix the H atoms, clarify the ambiguities and increase the accuracy of this work.

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Quinoline-2-carboxamide Hemihydrate

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Abstract. $C_{10}H_8N_2O.\frac{1}{2}H_2O$, orthorhombic, *Pbca*, a = 11·885 (2), b = 39·30 (2), c = 7·6176 (8) Å, Z = 16, D_m = 1·34, D_c = 1·35 g cm^{-3}, R = 0·052. The planarity of the quinoline ring is different for the two independent molecules. Hydrogen bonding is discussed.

Introduction. Crystals suitable for single-crystal X-ray analysis were obtained by recrystallization from methanol–water solution. A crystal with the dimensions 0·1 × 0·1 × 0·07 mm was used for measurements on a Syntex $P2_1$ diffractometer. Cell dimensions were determined from a least-squares fit of 2θ, ω and χ values for 15 reflexions. Measurements of the intensities were carried out in the θ–2θ mode ($2\theta_{\max}$ = 115°) with graphite-monochromated Cu radiation. A variable 2·95–29·3° min^{-1} scan rate was used. Application of the rejection criterion $I < 1\cdot96\sigma(I)$ yielded 1504 independent reflexions for use in the analysis.

The structure was solved by direct methods. 242 reflexions with $E \geq 1\cdot6$ were used as input to the program *MULTAN*. An E map calculated for the set with the highest absolute figure of merit gave the positions of all non-hydrogen atoms. Refinement of the structure was carried out by the full-matrix least-squares method. All H atoms, except those of the water molecule, were found from a difference Fourier synthesis and included in the refinement. The isotropic temperature factor assigned to a H atom was one unit greater than the isotropic temperature factor of the heavy atom to which it was bonded. The function minimized in full-matrix least-squares calculations was $\Sigma w(F_o - F_c)^2$. The weighting scheme was based on counting statistics, $w = (\sigma^2 + c^2F^2)^{-1}$; c was equal to zero until the refinement ceased. Least-squares analysis of the expression $\sigma^2 + c^2F^2 = (\Delta F)^2$ gave a value of c = 0·035. This value was applied in three more cycles of least-squares refinement. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$ are 0·052 and 0·062 respectively; the goodness of fit, *i.e.* $[\Sigma w(F_o - F_c)^2/(N_o - N_v)]^{1/2}$, is 1·19, where N_o is the number of observations and N_v the number of variables.

Table 1. *Fractional coordinates of non-hydrogen atoms*

The coordinates are in fractions of unit-cell edges × 10^4.

	x	y	z
C(2)	1417 (3)	2100 (1)	1279 (5)
C(3)	347 (3)	2138 (1)	532 (5)
C(4)	−62 (4)	2458 (1)	289 (6)
C(5)	210 (4)	382 (1)	652 (6)
C(6)	863 (4)	3345 (1)	1203 (6)
C(7)	1948 (4)	3281 (1)	1889 (6)
C(8)	2336 (4)	2957 (1)	2022 (5)
C(9)	1649 (3)	2679 (1)	1502 (5)
C(10)	571 (3)	2742 (1)	789 (5)
C(11)	1880 (3)	1751 (1)	1619 (5)
N(1)	2063 (3)	2357 (1)	1753 (4)
N(2)	2856 (3)	1745 (1)	2483 (5)
O(1)	1383 (2)	1492 (1)	1158 (4)
C(2′)	3711 (3)	4530 (1)	3469 (5)
C(3′)	4715 (3)	4572 (1)	2511 (5)
C(4′)	5109 (3)	4892 (1)	2243 (5)
C(5′)	4856 (4)	5513 (1)	2715 (6)
C(6′)	4236 (4)	5770 (1)	3404 (6)
C(7′)	3246 (4)	5705 (1)	4312 (6)
C(8′)	2864 (4)	5379 (1)	4520 (5)
C(9′)	3499 (3)	5103 (1)	3829 (5)
C(10′)	4510 (3)	5172 (1)	2905 (5)
C(11′)	3282 (4)	4123 (1)	3808 (5)
O(1′)	3730 (3)	3925 (1)	3122 (4)
N(2′)	2412 (4)	4154 (1)	4897 (6)
N(1′)	3112 (3)	4781 (1)	4110 (4)
O(W)	4193 (2)	1259 (1)	4581 (4)