Summary

For the lizardite variety of serpentine from Kennack Cove, Cornwall, X-ray diffraction single-crystal methods confirm the basic serpentine structure and show that the crystals are disordered in three different ways. (1) Non-Bragg diffraction maxima and the intensities of other reflexions show that individual serpentine layers may be rotated by $\pm 60°$ or 180°; these layers are most probably stacked in domains some of which are in one-layer sequences in either orientation, and others in alternating sequences with a two-layer repeat. The latter exhibit sequences containing mistakes, the probability of which varies from one crystal to another, and possibly also from one domain to another within a single crystal. (2) Reflexions with $k \neq 3m$, which are streaked parallel to **c***, show that layers may be displaced by $\pm b/3$, and the probability of a stacking mistake is approximately 0·4. (3) Reflexions are spread along powder arcs indicating considerable curvature of the crystal on a macroscopic scale, so that its habit approximates to a spherical cap.

The 'average' structure (*i.e.* layer shifts and rotations averaged over the whole crystal) has trigonal symmetry, but the ortho-hexagonal cell with $b = a\sqrt{3}$ is used for its description.

In view of the above results, it may be conjectured that different lizardite specimens may exhibit translational and rotational disorder to varying degrees, and also that multi-layered regular sequences additional to those already described for serpentine structures (*e.g.* 6-layered, Zussman & Brindley, 1957; Gillery, 1959; Lapham 1961) may occur. The Kennack specimen is exceptional in that other lizardites are too fine-grained for single-crystal X-ray work. In powder patterns of the fine lizardites, non-Bragg maxima and other diffuse reflexions may be too weak to be observed, but the relative intensities of the main reflexions might be expected to show some variations. Such effects, however, would be reduced in powder patterns because of the coincidence of *hkl* and $\bar{h}kl$ reflexions owing to the dimensional symmetry of the crystal lattice.

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References

GILLERY, G. H. (1959). *Amer. Min.* **44**, 143.
HENDRICKS, S. B. (1940). *Phys. Rev.* **57**, 448.
KUNZE, G. (1956). *Z. Kristallogr.* **108**, 82.
KUNZE, G. (1958). *Z. Kristallogr.* **110**, 282.
KUNZE, G. (1961). *Fortschr. Min.* **39**, 206.
LAPHAM, D. M. (1961). *Amer. Min.* **46**, 168.
MIDGLEY, H. G. (1951). *Miner. Mag.* **29**, 526.
WHITTAKER, E. J. W. (1956*a*). *Acta Cryst.* **9**, 855.
WHITTAKER, E. J. W. (1956*b*). *Acta Cryst.* **9**, 862.
WHITTAKER, E. J. W. & ZUSSMAN, J. (1956). *Miner. Mag.* **31**, 107.
WILSON, A. J. C. (1962). *X-ray Optics*. London: Methuen.
ZUSSMAN, J. & BRINDLEY, G. W. (1957). *Amer. Min.* **42**, 666.

Acta Cryst. (1965). **19**, 389

The Crystal Structure of Bisnitratodiaquodioxouranium(VI) Tetrahydrate (Uranyl Nitrate Hexahydrate)

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The crystal structure of uranyl nitrate hexahydrate has been refined in three dimensions. The uranium atom is 8-coordinate, with the two nitrate ions (as bidentate ligands) and the two water molecules coordinated in the plane perpendicular to the uranyl group. The molecule is involved with the water of crystallization in an extensive hydrogen-bonding system, which apparently causes some distortion from the ideal molecular shape.

The structure determination of the hexahydrate of uranyl nitrate by Fleming & Lynton (1960) has shown the compound to be correctly formulated $[UO_2(NO_3)_2(H_2O)_2]4H_2O$, with the nitrate ions acting as bidentate chelating groups. The structure was studied in projection, and only in one such projection was satisfactory refinement possible. The reported parameters are then at best of low precision, and many apparently interesting features of the molecule, *e.g.* the non-linear uranyl ion, must be treated with some reserve. We have redetermined this structure, and have refined the parameters using three-dimensional procedures.

Experimental

Suitable crystals were available from a commercial sample without recrystallization. The dimensions of the orthorhombic unit cell were obtained from Weissenberg photographs by the method of Main & Woolfson (1963) as $a = 13{\cdot}18 \pm 0{\cdot}01$, $b = 8{\cdot}00 \pm 0{\cdot}02$, $c = 11{\cdot}47 \pm$

0·01 Å, where the errors quoted are standard deviations. These results agree well with those given by Pauling & Dickenson (1924), *viz.* $a=13{\cdot}15$, $b=8{\cdot}02$, $c=11{\cdot}42$ Å. The observed density (Pauling & Dickenson) was 2·72 g.cm^{-3}, which may be compared with 2·770 calculated (from our cell parameters) for 4 molecules per unit cell.

Reflexions were systematically absent for *hkl* with $h+k$ odd, and additionally for *h*0*l* with *l* odd, whence the possible space groups are *Cmcm*, $Cmc2_1$ and *C*2*cm*. Sasvari (1957) has observed the crystals to be pyroelectric and deduced the space group as $Cmc2_1$. The structure analysis has confirmed this result.

Intensity data were collected by visual estimation from Weissenberg photographs about all three principal axes (*nkl*, $n=0-6$; *hnl*, $n=0-5$; *hkn*, $n=0-3$). Crystals were photographed in narrow-walled glass capillaries to prevent the decomposition which otherwise occurred under X-radiation.

The crystals used were bounded by faces normal to the principal axes and were of the following dimensions: for rotation about *a*, 0·065 × 0·130 × 0·130 mm; for rotation about *b*, 0·091 × 0·156 × 0·143 mm; for rotation about *c*, 0·130 × 0·191 × 0·130 mm. The *a*-axis data were corrected for absorption by approximating to a sphere and using the corrections given by Bond (1959). The remaining data were corrected following the procedure of Busing & Levy (1957), using a program written by B. M. Craven (unpublished) for the IBM 1620 computer.

The data were correlated by minimizing the function $\Sigma\, w_{hij}\Delta^2_{hij}$ where $\Delta_{hij}=\log k_i F_{hi}-\log k_j F_{hj}$ and F_{hi} is the value of F_{hkl} in the *i*th data zone. The method of setting up and solving the least-squares equations will be described separately. It was assumed that a constant percentage error exists in measured intensities except for those less than some limit I_1, which in this case was taken as the highest intensity that could be accurately measured from the top film of the multi-pack. A constant error was assumed for intensities between I_1 and I_2, taken as the region of the top film for which a second measurement may be obtained from the second film. The error was assumed to increase by a factor $(I_2/I)^{\frac{1}{2}}$ where the intensity was less than I_2, to allow for the difficulty in assessment of these values. The variance in $I^{\frac{1}{2}}$ was then proportional to mI, where $m=1$ for $I>I_1$, $m=I_1/I$ where $I_1>I>I_2$, and $m=I_1I_2^{\frac{1}{2}}I^{-3/2}$ where $I_2>I$. As the corrections to the intensity for the absorption, Lorentz and polarization factors are multiplicative, $\sigma^2(F)$ is similarly proportional to mF^2. The weighting factor, W_{hij}, was then taken as $1/(m_{hi}+m_{hj})$, the mean value of F_{hkl} after application of the scale factors as $\sum_i m_{hi}^{-1}F_{hi}/\Sigma m_{hi}^{-1}$, and the variance in F_{hkl} as $\sum_i m_{hi}^{-1}F_{hi}^2/(\Sigma m_{hi}^{-1})^2$. An assessment of the success of the correlation is given by the value of 0·092 for the function $\Sigma||F_{hi}|-|F_{hj}||/\frac{1}{2}\Sigma||F_{hi}|+|F_{hj}||$.

Determination of the structure

It was obvious from the distribution of intensities that the uranium atoms do not occupy positions (*a*) or (*b*) of the space group *Cmcm*, or (*a*) of *C*2*cm*, and the possible locations are then (*c*) of *Cmcm*, (*a*) of $Cmc2_1$, and (*b*) of *C*2*cm*. The coordinates $0, y, \frac{1}{4}$ describe all of these positions. It was noted that reflexions for which $h+2l=4n$ were very intense, and those for which $h+2l=4n+2$ generally weak (222 being a notable exception), whence the uranium atom was placed at $0, \frac{1}{8}, \frac{1}{4}$. Structure factors were calculated on the basis of this atom alone, using the scattering curve of Thomas, Umeda & King (1958) with a real dispersion correction of −6·8 (Roof, 1961), and an initial reliability index of 0·137 was obtained for those terms to which the uranium contributed. The *R* index was not then very sensitive to the details of the light atom arrangement, and it was found that the value of $\Sigma w(\Delta F)^2$, relative to the value from this uranium-only calculation, was a more useful criterion of the progress of refinement. This ratio will be referred to as *R*′.

A subsequent difference Fourier synthesis had of necessity symmetry *Cmcm*, but it was readily apparent that the mirror plane at $z=\frac{1}{4}$ was false, *i.e.* that the correct space group was $Cmc2_1$, and that the structure of the complex molecule was essentially as described by Fleming & Lynton (1960). The ambiguity in the *z* parameter of the two uncoordinated water molecules was resolved by virtue of the markedly better agreement obtained in one situation for those structure amplitudes to which the uranium atom makes no contribution. Three least-squares cycles, in which the uranium atom was permitted anisotropic thermal parameters and the light atoms isotropic parameters, reduced *R*′ to 0·40. The weighting factors were obtained from the variance in *F*, estimated as above. Further refinement cycles gave no improvement, but large oscillating positional shifts, in excess of the standard deviations, were still being predicted for the light atoms. The *z* coordinate for the non-coordinated water oxygen atoms were interchanged, to test the alternative arrangement again, but *R*′ increased to 0·60, and the agreement for the reflexions for which $h+l=4n+2$ was obviously much worse.

Consideration was then given to the effect of the anomalous dispersion term, $\Delta f''=16{\cdot}0$ (Roof, 1961). The structure factors may be written $F_{hkl}=A_U+A_L+i(B_U+B_L)$, the subscripts *U* and *L* referring to the uranium and light atoms respectively. As the uranium atoms are centrically related $B_U=A_U(\Delta f''/f)$. Where *F*′ is the calculated structure factor neglecting anomalous dispersion, $|F_{hkl}|^2=|F'|^2+B_U^2+2B_UB_L$ and $F_{hkl}|^2=|F'|^2+B_U^2-2B_UB_L$. No attempt had been made to differentiate reflections *hkl* and *hk*$\bar{l}$, and it was assumed that the effect of the B_UB_L term had been averaged out in the data collection. The correction was made to the observed amplitude, *i.e.* $|F_o'|=(|F_o|^2-B_U^2)^{\frac{1}{2}}$, giving terms that are more correctly those that would

Table 1. *Observed and calculated structure factors*

The values listed as F_o are those corrected for anomalous dispersion, and described in the text as F_o'

H	K	L	FO	FC		AC	BC
4	0	0	303.3	417.5		417.5	0.0
6	0	0	236.2	302.4		302.4	0.0
8	0	0	153.7	182.7		182.7	0.0-
10	0	0	180.9	229.8		229.8	0.0-
12	0	0	125.1	152.6		152.6	0.0-
14	0	0	97.3	120.7		120.7	0.0
16	0	0	69.2	79.3		79.3	0.0
3	1	0	148.3	182.0		182.0	0.0
5	1	0	154.6	148.0		148.0	0.0
7	1	0	149.2	159.2		159.2	0.0
9	1	0	90.4	95.0		95.0	0.0
11	1	0	90.5	96.8		96.8	0.0
13	1	0	58.6	67.4		67.4	0.0
15	1	0	45.6	47.1		47.1	0.0
0	2	0	29.9	22.0	*	22.0-	0.0
2	2	0	24.5	11.5	*	11.5-	0.0
4	2	0	24.8	18.3	*	18.3-	0.0
6	2	0	27.6	15.7	*	15.7-	0.0
8	2	0	28.3	10.5	*	10.5-	0.0
10	2	0	25.8	10.6	*	10.6-	0.0
12	2	0	24.1	5.6	*	5.6-	0.0
14	2	0	19.7	5.9	*	5.9-	0.0
16	2	0	12.4	3.8	*	3.8-	0.0
1	3	0	201.7	229.3		229.3-	0.0-
3	3	0	129.3	137.4		137.4-	0.0-
5	3	0	177.2	198.9		198.9-	0.0-
7	3	0	120.5	118.8		118.8-	0.0-
9	3	0	120.3	114.5		114.5-	0.0-
11	3	0	95.9	99.1		99.1-	0.0-
13	3	0	63.4	68.7		68.7-	0.0-
15	3	0	57.0	55.3		55.3-	0.0-
0	4	0	191.7	257.0		257.0-	0.0-
2	4	0	222.1	266.6		266.6-	0.0-
4	4	0	154.4	156.1		156.1-	0.0-
6	4	0	150.7	150.3		150.3-	0.0-
8	4	0	141.5	125.3		125.3-	0.0-
10	4	0	119.0	109.0		109.0-	0.0-
12	4	0	108.3	114.0		114.0-	0.0-
14	4	0	73.1	68.0		68.0-	0.0-
1	5	0	96.4	101.9		101.9-	0.0
3	5	0	84.3	78.8		78.8-	0.0
5	5	0	127.6	106.7		106.7-	0.0
7	5	0	91.3	77.8		77.8-	0.0
9	5	0	87.2	65.7		65.7-	0.0
11	5	0	62.5	56.0		56.0-	0.0
13	5	0	43.4	39.0		39.0-	0.0
0	6	0	34.5	7.5	*	7.5	0.0
2	6	0	34.8	20.0	*	20.0	0.0
4	6	0	39.5	11.8	*	11.8	0.0
6	6	0	39.4	16.0	*	16.0	0.0
8	6	0	36.3	14.2	*	14.2	0.0
10	6	0	25.1	7.5	*	7.5	0.0
12	6	0	14.6	10.1	*	10.1	0.0
1	7	0	90.4	88.9		88.9	0.0
3	7	0	78.6	74.4		74.4	0.0
5	7	0	73.4	70.5		70.5	0.0
7	7	0	71.3	62.8		62.8	0.0
9	7	0	63.2	50.6		50.6	0.0
11	7	0	51.7	49.8		49.8	0.0
0	8	0	112.3	124.5		124.5	0.0-
2	8	0	97.4	94.2		94.2	0.0-
4	8	0	82.1	88.9		88.9	0.0-
6	8	0	78.4	77.7		77.7	0.0-
8	8	0	67.6	60.5		60.5	0.0-
10	8	0	55.9	63.8		63.8	0.0-
1	9	0	46.3	45.3		45.3	0.0-
3	9	0	45.7	41.2		41.2	0.0-
5	9	0	50.1	45.7		45.7	0.0-
7	9	0	39.3	37.7		37.7	0.0-
0	10	0	14.5	16.3	*	16.3-	0.0
2	10	0	13.3	9.2	*	9.2-	0.0
4	10	0	9.0	13.5	*	13.5-	0.0
3	1	1	156.8	180.4		176.2-	38.9
5	1	1	201.4	181.2		176.1-	42.8-
7	1	1	148.1	154.6		154.5-	5.3
9	1	1	102.6	103.4		103.0-	9.1-
11	1	1	94.6	100.4		100.2-	6.5
13	1	1	61.1	70.1		69.7-	7.4
15	1	1	49.5	51.3		51.3-	0.0
0	2	1	252.8	301.1		300.5-	18.2-
2	2	1	177.0	237.0		236.2-	19.4
4	2	1	243.2	302.5		302.4-	6.3-
6	2	1	272.3	310.9		310.9-	3.7-
8	2	1	185.3	199.9		199.8-	4.5
10	2	1	135.8	154.9		154.8-	4.0-
12	2	1	90.8	108.2		108.2-	2.2
14	2	1	70.3	76.3		76.3-	1.3-
16	2	1	63.5	66.2		66.2-	0.5-
1	3	1	186.0	202.8		195.8	52.8
3	3	1	134.4	140.9		140.1-	15.2-
5	3	1	166.7	162.7		159.4-	32.8
7	3	1	129.3	118.5		115.2-	27.6-
9	3	1	102.4	96.3		95.1-	15.0
11	3	1	88.2	86.7		86.5-	5.8
13	3	1	59.0	61.7		61.6-	4.3
15	3	1	51.0	47.9		47.4-	6.7
0	4	1	33.2	19.2	*	15.5	11.3
2	4	1	46.3	46.1		26.8	37.5
4	4	1	31.7	25.7		13.1	22.1
4	4	1	36.0	25.7	*	13.1	22.1
6	4	1	35.9	27.2		14.9	22.8
6	4	1	30.8	27.2	*	14.9	22.8
8	4	1	35.3	23.8	*	13.4	19.7
10	4	1	30.7	10.7	*	8.7	6.3
12	4	1	25.0	13.6	*	11.0	8.0
14	4	1	18.1	6.4	*	5.8	2.6
1	5	1	[illegible]	136.1		136.1	2.7-
3	5	1	109.6	102.5		102.1	8.9
5	5	1	151.6	139.7		139.3	11.2
7	5	1	116.8	97.8		96.6	15.1
9	5	1	106.4	84.6		84.5	4.3
11	5	1	75.5	71.3		71.3	2.2
13	5	1	57.1	50.4		50.4	0.6
0	6	1	122.7	147.8		147.0	15.2-
2	6	1	127.0	139.7		139.5	6.6
4	6	1	152.5	150.2		150.1	6.7-
6	6	1	169.7	154.2		154.2	1.3-
8	6	1	152.1	115.1		115.1	1.7
10	6	1	101.1	90.6		90.5	5.2-
12	6	1	61.7	70.1		70.1	1.8
1	7	1	71.9	71.0		71.0	0.6
3	7	1	55.4	58.4		57.5	10.0-
5	7	1	71.7	60.2		57.7	17.0
7	7	1	53.5	47.6		47.4	4.7-
9	7	1	46.7	40.4		40.0	5.6
11	7	1	38.3	38.2		38.1	2.2-
0	8	1	31.2	23.6	*	21.1-	10.6-
2	8	1	30.6	13.8	*	12.9-	4.8-
4	8	1	28.6	18.7	*	15.2-	10.9-
6	8	1	26.4	16.5	*	13.2-	9.9-
8	8	1	18.5	11.3	*	9.3-	6.4-
10	8	1	9.6	12.7	*	11.0-	6.4-
1	9	1	66.2	62.4		62.2-	4.9
3	9	1	63.3	60.4		60.3-	3.7
5	9	1	66.7	58.8		58.8-	0.4
7	9	1	48.1	54.3		54.3-	1.1
0	10	1	47.2	54.3		54.2-	2.7-
2	10	1	46.3	49.5		49.5-	2.2
0	0	2	269.1	358.7		358.3-	16.0-
2	0	2	231.0	355.9		355.9-	5.7
4	0	2	196.7	212.4		212.4-	1.1
6	0	2	216.9	214.4		214.4-	4.4-
8	0	2	152.1	164.5		164.5-	1.3
10	0	2	124.3	141.0		140.9-	4.2-
12	0	2	120.6	139.5		139.5-	3.6-
14	0	2	74.3	84.3		84.3-	0.9-
16	0	2	63.4	69.2		69.2-	1.7-
1	1	2	185.2	222.7		215.3-	56.8-
3	1	2	127.0	136.9		131.7-	37.3-
5	1	2	211.2	206.8		201.1-	48.1
7	1	2	133.5	125.1		125.0-	6.0
9	1	2	105.5	110.0		109.4-	11.5
11	1	2	93.0	94.5		93.8-	11.2-
13	1	2	60.7	64.4		63.5-	10.7-
15	1	2	52.4	51.0		51.0-	1.6-
0	2	2	27.0	31.5	*	1.8	31.4
2	2	2	128.0	142.4		10.3	142.0
4	2	2	45.2	43.4		4.7	43.1
6	2	2	55.8	45.7		8.7	44.9
8	2	2	60.5	49.0		6.8	48.5
10	2	2	27.3	12.0	*	3.2	11.6
12	2	2	33.2	29.4		5.1	29.0
14	2	2	20.3	8.6	*	1.7	8.4
16	2	2	11.7	10.1	*	2.6	9.8
1	3	2	193.5	213.2		207.0	51.2
3	3	2	161.0	175.5		175.4	5.7-
5	3	2	165.6	164.0		164.0	1.6
7	3	2	152.1	147.9		145.9	24.1-
9	3	2	114.7	102.9		102.9	2.8
11	3	2	98.4	97.5		97.1	8.9
13	3	2	69.1	69.1		68.8	6.8
15	3	2	53.8	50.2		50.0	4.7
0	4	2	216.7	297.5		297.5	1.9
2	4	2	164.6	179.9		179.4	12.9-
4	4	2	175.0	186.1		186.0	6.7-
6	4	2	171.3	162.3		162.2	4.8-
8	4	2	123.0	111.5		111.3	6.8-
10	4	2	131.8	126.1		126.1	0.5-
12	4	2	90.9	93.2		93.2	2.2-
14	4	2	74.7	72.1		72.1	1.2-
1	5	2	109.3	116.7		116.7	2.0
3	5	2	112.5	107.2		103.9	26.3-
5	5	2	127.9	110.1		107.8	22.3-
7	5	2	115.3	98.2		92.5	33.0-
9	5	2	89.3	70.6		69.3	13.3-
11	5	2	69.0	61.5		61.2	5.6-
13	5	2	51.7	43.9		43.7	3.8-
0	6	2	37.6	45.8		25.5-	38.0-
2	6	2	35.9	14.9	*	12.2-	8.5-
4	6	2	36.5	26.3	*	20.2-	16.9-
6	6	2	38.2	19.5	*	18.1-	7.3-
8	6	2	37.8	11.8	*	11.6-	2.3-
10	6	2	26.3	17.8	*	13.3-	11.9-
12	6	2	15.5	8.1	*	7.2-	3.7-
1	7	2	103.3	107.5		107.4-	5.2-
3	7	2	92.0	88.6		88.6-	2.8
5	7	2	94.9	93.3		93.0-	7.7
7	7	2	77.0	74.3		73.9-	7.4
9	7	2	73.1	63.2		63.1-	3.2
11	7	2	53.0	56.2		56.2-	1.4-
0	8	2	102.9	108.1		108.1-	2.4
2	8	2	97.5	101.1		101.1-	3.0-
4	8	2	80.2	86.6		86.6-	2.3
6	8	2	75.8	81.2		81.2-	0.4
8	8	2	62.1	66.5		66.5-	0.3-
10	8	2	43.3	59.1		59.1-	1.4
1	9	2	45.9	43.3		42.6-	7.6-
3	9	2	41.7	40.4		40.2-	3.6-
5	9	2	44.9	40.5		40.5-	0.6
7	9	2	31.8	36.0		36.0-	1.0
0	10	2	13.8	13.1	*	10.6	7.7
2	10	2	12.7	16.0	*	13.5	8.6
1	1	3	233.0	252.1		241.6	72.1-
3	1	3	121.2	134.6		133.8	14.7-
5	1	3	217.3	220.2		219.4	18.4
7	1	3	141.4	120.8		117.1	29.7
9	1	3	115.9	118.6		118.6	2.5-
11	1	3	95.0	97.9		97.4	9.5-
13	1	3	62.8	67.6		66.7	10.9-
15	1	3	60.1	55.6		55.3	5.8-
0	2	3	214.3	230.2		230.2	2.2-
2	2	3	161.1	188.1		187.9	8.0-
4	2	3	170.7	186.8		186.7	5.8-
6	2	3	196.7	198.8		198.8	1.8
8	2	3	145.0	139.7		139.6	4.9-
10	2	3	120.9	122.8		122.8	2.3-
12	2	3	94.2	101.5		101.5	0.2
14	2	3	63.0	69.5		69.5	1.4-
16	2	3	52.7	58.6		58.6	0.6
1	3	3	177.2	178.8		175.0	36.5-
3	3	3	147.7	148.1		146.9	19.2-
5	3	3	145.5	142.4		137.9	35.7
7	3	3	141.9	122.0		121.2	14.3
9	3	3	102.1	86.8		86.6	5.6
11	3	3	88.1	82.9		82.5	8.1-
13	3	3	61.6	59.5		58.6	10.1-
15	3	3	45.7	42.6		42.5	2.8-
0	4	3	41.6	38.8		38.5-	4.5-
2	4	3	31.4	4.9	*	0.7-	4.8-
4	4	3	30.0	25.9		20.6-	15.7-
4	4	3	37.0	25.9	*	20.6-	15.7-
6	4	3	38.1	22.4		14.1-	17.4-
6	4	3	34.6	22.4	*	14.1-	17.4-
8	4	3	36.0	12.2	*	4.8-	11.2-
10	4	3	30.8	15.1	*	13.7-	6.3-
12	4	3	24.8	4.4	*	3.9-	2.0-
14	4	3	17.1	6.9	*	6.6-	1.9-
1	5	3	148.1	154.1		154.1-	1.5-
3	5	3	159.4	154.8		154.4-	11.0-
5	5	3	143.3	123.1		118.6-	33.1-
7	5	3	151.0	129.9		127.7-	23.9-
9	5	3	[illegible]	83.0		81.8-	14.1-
11	5	3	89.9	80.0		79.8-	5.2-
13	5	3	70.0	58.5		58.5-	1.6-
0	6	3	137.8	166.1		166.1-	0.5-
2	6	3	123.1	130.1		129.9-	7.8
4	6	3	138.5	137.8		137.8-	2.2
6	6	3	141.7	130.8		130.8-	0.5
8	6	3	127.5	96.8		96.7-	4.2
10	6	3	99.6	89.3		89.3-	0.9
12	6	3	68.2	67.3		67.3-	1.8
1	7	3	79.4	82.3		80.4-	17.5
3	7	3	75.5	69.0		68.8-	5.2
5	7	3	79.1	69.5		69.5-	0.7
7	7	3	72.6	56.9		56.7-	5.1-
9	7	3	57.2	47.8		47.6-	4.2
11	7	3	45.3	42.2		41.8-	6.1
0	8	3	30.3	19.6	*	13.1	14.6
2	8	3	29.6	27.7	*	21.7	17.2
4	8	3	27.3	24.0	*	13.2	20.1
6	8	3	24.9	25.1	*	14.3	20.6
8	8	3	16.9	21.4	*	13.5	16.6
1	9	3	68.9	68.5		68.5	2.6-
3	9	3	60.1	55.4		55.4	0.6
5	9	3	68.9	65.3		65.2	3.9
7	9	3	43.2	47.2		47.0	4.5
0	0	4	155.8	175.6		175.6	1.4-
2	0	4	137.4	145.3		143.5	22.7-
4	0	4	174.5	163.0		162.7	9.9-
6	0	4	186.5	187.2		187.2	0.3-
8	0	4	150.1	129.8		129.5	8.3-
10	0	4	102.3	111.5		111.5	1.0-
12	0	4	74.5	91.9		91.9	2.8-
14	0	4	58.3	63.1		63.0	2.8-
16	0	4	46.6	55.2		55.2	1.3-
1	1	4	226.6	226.7		210.0	85.5
3	1	4	152.4	157.5		157.4	4.7-
5	1	4	192.2	188.0		187.2	16.9
7	1	4	161.6	138.2		134.5	31.6-
9	1	4	115.0	107.5		107.3	6.7
11	1	4	89.6	93.2		92.3	12.6
13	1	4	62.5	64.7		64.2	8.3
15	1	4	53.7	50.4		50.0	6.5
0	2	4	93.1	84.5		14.0-	83.3-
2	2	4	59.8	40.1		0.8	40.1
4	2	4	31.3	30.4	*	7.5-	29.5-
6	2	4	34.2	8.1	*	5.9-	5.6-
8	2	4	39.6	10.9	*	1.8-	10.7
10	2	4	31.1	22.6	*	4.9-	22.1-
12	2	4	26.9	4.6	*	1.5-	4.4
14	2	4	20.4	10.6	*	2.1-	10.4-
1	3	4	179.3	173.7		171.3-	28.9-
3	3	4	155.4	146.6		146.1-	11.9-
5	3	4	160.1	156.9		154.4-	28.0
7	3	4	149.3	128.0		127.8-	7.3
9	3	4	103.6	94.9		94.6-	8.0
11	3	4	93.0	84.7		84.2-	9.3-
13	3	4	70.6	60.0		59.4-	8.2-
15	3	4	47.8	45.0		45.0-	1.8-
0	4	4	178.6	207.7		207.7-	3.6
2	4	4	146.4	167.4		167.4-	0.4
4	4	4	171.4	180.4		180.3-	5.4
6	4	4	176.7	177.8		177.8-	2.7-
8	4	4	132.6	128.4		128.4-	1.1
10	4	4	102.3	112.5		112.5-	2.0
12	4	4	87.0	85.9		85.9-	1.7-
14	4	4	65.2	63.1		63.0-	2.8
1	5	4	125.9	120.7		120.6-	4.0-
3	5	4	115.3	104.8		104.6-	6.4
5	5	4	124.5	109.2		104.8-	30.8
7	5	4	114.4	89.3		87.5-	17.9
9	5	4	75.6	70.2		68.4-	15.9
11	5	4	78.1	60.4		60.4-	2.4
13	5	4	59.1	44.0		44.0-	1.0
0	6	4	42.9	21.7	*	21.7	0.6
2	6	4	41.8	31.3	*	20.1	24.0
4	6	4	39.1	18.6	*	18.6	0.8-
6	6	4	38.3	17.9	*	17.8	1.8
1	7	4	109.9	107.3		105.4	20.1
3	7	4	95.5	94.8		94.3	10.1
5	7	4	100.0	97.6		97.4	5.9
0	8	4	90.0	92.4		92.3	3.2
2	8	4	87.9	84.8		84.4	8.0-
4	8	4	77.7	83.8		83.8	1.3-
6	8	4	84.2	81.2		81.2	1.4-
1	9	4	42.5	40.5		39.8	7.3-
3	9	4	38.6	37.6		35.6	12.0-
5	9	4	37.5	37.7		35.3	13.1-
1	1	5	215.0	205.2		203.3-	28.0
3	1	5	188.3	187.7		187.6-	4.7
5	1	5	155.6	149.9		149.3-	13.6-
7	1	5	161.3	151.5		150.2-	19.9-
9	1	5	107.2	98.9		98.9-	0.7
11	1	5	89.8	96.4		96.4-	1.8
13	1	5	65.9	69.5		69.3-	4.7
15	1	5	47.8	48.4		48.3-	2.4
0	2	5	247.0	304.8		304.7-	7.2-
2	2	5	193.8	223.0		223.0-	1.9-
4	2	5	178.5	190.2		190.1-	6.8
6	2	5	163.8	168.8		168.8-	0.2-
8	2	5	133.4	125.3		125.2-	6.0
10	2	5	127.0	129.4		129.4-	2.4
12	2	5	103.2	107.0		107.0-	2.2-
14	2	5	78.7	76.5		76.5-	1.9
1	3	5	148.4	139.0		138.5-	12.2
3	3	5	117.7	104.0		102.5-	17.5
5	3	5	148.7	131.9		128.6-	29.3-
7	3	5	105.4	89.6		89.6-	2.8-
9	3	5	96.2	79.3		79.2-	4.4-
11	3	5	75.7	67.1		66.9-	4.9
13	3	5	56.4	47.8		47.2-	7.7
15	3	5	35.6	37.6		37.6-	1.9
0	4	5	41.8	11.4	*	8.1	8.0-
2	4	5	52.7	30.2		24.5	17.7-
4	4	5	39.2	12.0	*	11.8	1.9-
6	4	5	39.6	14.7	*	14.7	1.2
8	4	5	42.6	14.2	*	14.2	0.9-
10	4	5	33.0	7.1	*	6.7	2.4
12	4	5	25.7	9.9	*	9.8	1.1-
14	4	5	15.1	4.6	*	4.4	1.5
1	5	5	142.4	137.1		136.9	8.1
3	5	5	111.7	95.9		95.1	12.2
5	5	5	130.8	125.0		122.9	22.8
7	5	5	100.8	80.3		77.9	19.3
9	5	5	89.8	79.8		79.1	10.8
11	5	5	95.3	66.8		66.4	7.2
13	5	5	60.1	48.1		48.0	3.7
0	6	5	123.1	139.1		138.8	8.9
2	6	5	112.8	123.5		123.2	8.0-
4	6	5	100.7	102.7		102.7	0.5-
6	6	5	97.5	94.9		94.9	0.4-
1	7	5	84.7	76.1		71.3	26.6-
3	7	5	66.4	67.8		66.0	15.5-
5	7	5	73.0	66.8		64.9	16.0-
0	8	5	32.5	23.6	*	19.7-	13.0-
2	8	5	31.1	20.8	*	11.0-	17.6-
4	8	5	27.3	22.9	*	15.4-	16.9-
6	8	5	24.1	22.3	*	13.5-	17.7-
1	9	5	59.2	58.4		57.6-	9.9-
3	9	5	50.5	55.4		54.6-	9.5-
5	9	5	43.2	47.5		45.9-	12.4-
0	0	6	235.9	255.9		255.8-	5.9
2	0	6	162.4	152.4		152.3-	5.5
4	0	6	236.9	240.5		240.5-	3.2
6	0	6	219.2	232.2		232.0-	10.3-
8	0	6	151.0	150.3		150.3-	0.9
10	0	6	127.0	135.7		135.7-	2.7
12	0	6	66.0	81.5		81.5-	0.2-
14	0	6	69.0	68.4		68.2-	4.6
1	1	6	193.2	170.0		170.0-	0.2-
3	1	6	177.0	159.5		159.3-	7.8
5	1	6	159.5	136.6		135.7-	15.7
7	1	6	149.6	130.2		130.0-	7.2
9	1	6	110.4	89.7		89.1-	10.4
11	1	6	80.5	83.1		83.1-	0.0
13	1	6	59.7	60.7		60.7-	1.1
15	1	6	38.4	43.8		43.7-	2.4
0	2	6	55.1	34.1	*	14.4	30.9-
2	2	6	39.9	18.3	*	14.9	10.6
4	2	6	50.0	19.8		11.7	16.0-
6	2	6	38.4	11.9	*	10.2	6.1-
8	2	6	42.0	8.8	*	8.3	2.8
10	2	6	33.1	9.8	*	6.7	7.2-
12	2	6	25.2	7.4	*	5.5	4.9
14	2	6	16.8	4.5	*	4.1	1.9-
1	3	6	133.9	134.1		132.7	19.4
3	3	6	111.2	100.2		100.2	1.8
5	3	6	148.0	134.6		134.0	12.2
7	3	6	108.6	92.4		92.4	1.7
9	3	6	100.9	82.4		82.2	5.0
11	3	6	75.0	69.0		68.5	8.0
13	3	6	55.6	49.0		48.8	4.6
0	4	6	124.9	144.8		144.4	11.0
2	4	6	154.7	169.4		169.2	8.3-
4	4	6	158.0	162.3		162.2	5.4
6	4	6	166.0	171.6		171.4	8.9
8	4	6	139.7	133.6		133.6	1.3-
10	4	6	85.9	94.8		94.7	3.5
12	4	6	91.4	80.4		80.4	1.2-
1	5	6	104.0	94.6		94.2	9.1-
3	5	6	81.8	77.4		74.9	19.5-
5	5	6	101.3	82.6		81.6	12.5-
7	5	6	75.4	64.3		62.0	17.1-
9	5	6	67.5	55.9		54.8	10.8-
11	5	6	65.2	49.1		48.7	6.1-
13	5	6	34.8	36.7		36.3	5.5-
0	6	6	41.6	31.7	*	[illegible]	27.8-
2	6	6	40.5	23.1	*	18.6-	13.7-
4	6	6	37.1	23.7	*	13.3-	19.6-
6	6	6	35.2	20.6	*	13.5-	15.5-
1	7	6	81.3	79.2		76.7-	19.8-
3	7	6	72.7	74.3		72.8-	15.0-
5	7	6	83.8	75.4		73.7-	16.0-
0	8	6	76.3	77.4		77.2-	5.9
2	8	6	68.1	67.0		66.9-	3.4
4	8	6	73.6	75.1		75.0-	4.6
6	8	6	73.8	73.4		73.4-	1.3
1	9	6	37.4	42.0		38.0-	17.9
3	9	6	34.3	37.7		32.7-	18.8
1	1	7	163.0	154.8		152.7	25.7

* = UNOBSERVED (FO = FMIN)

Table 1 (*cont.*)

H	K	L	FO	FC	AC	BC
3	1	7	148 5	122.2	122.1	3.6-
5	1	7	158.8	137.9	136.0	22.9
7	1	7	137.5	104.0	104.0	2.6-
9	1	7	110.2	88.5	88.0	9.0
11	1	7	76.9	76.6	76.1	8.4
13	1	7	59 2	55.2	55.0	4.3
0	2	7	205.6	272.0	270.4	29.1
2	2	7	191.9	219.5	219.5	2.1-
4	2	7	169.7	180.2	180.2	3.8
6	2	7	161.0	155.4	155.3	4.5
8	2	7	131.5	121.7	121.6	5.7-
10	2	7	127.3	119.2	119 1	5.4
12	2	7	99.1	100.2	100.2	2.5
14	2	7	62.5	71.6	71.6	1.2
1	3	7	112.4	104.1	100.0	29.1-
3	3	7	106.1	93.6	92.2	16.0-
5	3	7	116.5	100.8	93.0	38.9-
7	3	7	100.5	84.1	83.5	9.9-
9	3	7	80.8	67.1	62.8	23.5-
11	3	7	66.3	56.7	56.0	9.0-
13	3	7	45.3	41.3	40.7	7.3-
0	4	7	39 1	31.0	* 13.4-	28.0-
2	4	7	39 6	39.4	* 12.3-	37.4-
4	4	7	40.2	29.7	* 13.1-	26 7-
6	4	7	40.9	28.5	* 13.2-	25.3-
8	4	7	42.1	25.3	* 10 2-	23.2-
10	4	7	30.4	18.1	* 8.4-	16.0-
12	4	7	20.3	17.1	* 6.5-	15.8-
1	5	7	100.9	100.9	100.0-	13.2-
3	5	7	94.1	87.1	86.8-	7.4-
5	5	7	101.0	83.9	83.6-	7.0-
7	5	7	90.4	73.4	73.1-	6.6-
9	5	7	75.6	59.8	59 7-	3.7-
11	5	7	70.1	55.7	55 2-	7.3-
0	6	7	115.2	127.0	127.0-	3.5
2	6	7	99 8	109.7	109.7-	2.0-
4	6	7	87.1	93.6	93.4-	6.8
6	6	7	85.9	83.4	83.4-	2.7
1	7	7	57.0	57.9	55.4-	17.0
3	7	7	51.1	57.1	50.2-	27.2
5	7	7	57.1	56.2	55.1-	11.0
0	8	7	25.8	23.0	* 12.6	19.3
2	8	7	24.5	18.4	* 11.8	14.1
4	8	7	20.6	19.7	* 12.1	15.6
6	8	7	16.1	18 1	* 11.9	13.6
0	0	8	163.9	153.5	152.6	17.0
2	0	8	186 5	190 8	190.7	6.4-
4	0	8	180.2	169.3	169.0	9.2
6	0	8	179 5	178.2	177.6	14.3
8	0	8	159.2	141.6	141.6	0.0-
10	0	8	102.4	97.6	97.5	5.1
12	0	8	85.1	86.6	86.6	0.6
14	0	8	38.7	55.1	55.1	0.1-
1	1	8	163.8	131.1	126.6	34.0-
3	1	8	115.7	97.5	95.0	22.0-
5	1	8	139.4	113.3	112.8	11.0-
7	1	8	109 1	79.1	79.1	2.6-
9	1	8	97.0	74.7	73.6	12.8-
11	1	8	73.9	64.1	63.5	9.1-
13	1	8	48.6	47.6	46.7	9.3-
0	2	8	37.8	9 5	* 7.4-	6.0-
2	2	8	38.1	23.0	* 12.2-	19.5-
4	2	8	38.7	12.8	* 6.4-	11.1-
6	2	8	40.6	14.6	* 7.1-	12.7-
8	2	8	42.3	13.6	* 6.6-	11.9-
10	2	8	30 4	6.2	* 4.0-	4.8-
12	2	8	19.8	8.7	* 5.7-	6.6-
1	3	8	123.4	112.6	112.0-	11.4-
3	3	8	113.3	105.9	105.6-	8.2-
5	3	8	112.5	99.6	95.5-	28.2-
7	3	8	115.5	91.7	90.2-	16.7-
9	3	8	89.6	68.1	67.1-	11.9-
11	3	8	76.0	62.1	61.6-	7.7-
13	3	8	43.7	46.4	46.3-	3.2-
0	4	8	131.3	153.0	153.0-	1.4
2	4	8	107.6	114.9	114.8-	3.8
4	4	8	124.1	141.1	141.1-	1.2
6	4	8	130 3	134.0	133.9-	5.0-
8	4	8	100 6	98.1	98.1-	1.3
10	4	8	94.4	88 8	88.8-	1.1
12	4	8	52.7	59.6	59.6-	0.0
1	5	8	73.3	79.8	76.3-	23.4
3	5	8	66.5	71.1	67.3-	22.8
5	5	8	66.9	62.4	61.7-	9.3
7	5	8	67.3	55.8	54.6-	11.6
9	5	8	51.7	46.2	44.8-	11.4
11	5	8	43.8	42.8	41.5-	10.4
0	6	8	36.8	38.4	* 17.7	34.1
2	6	8	35.5	32.0	* 8.8	30.8
4	6	8	31.8	35.0	* 12.1	32.8
6	6	8	29 0	31.8	* 9.6	30.3
1	7	8	73.3	70.0	69.1	10.9
3	7	8	64.9	62.9	61.9	11.2
5	7	8	63.8	66.7	64.9	15.5
0	8	8	60.4	66.8	66.7	3.5-
2	8	8	62.7	69.0	68.8	5.3-
4	8	8	55.8	66.1	66.0	3.5-
1	1	9	117.5	105.8	102.9-	24.8-
3	1	9	98.5	86.3	85.2-	13.8-
5	1	9	119.4	100.8	100.7-	3.6
7	1	9	97.5	76.0	75.9-	4.1-
9	1	9	78.9	66.6	66.6-	0.1
11	1	9	62.3	56.3	55.3-	10 8-
0	2	9	134.2	157.8	157.7-	6.3-
2	2	9	136.8	141.0	141.0-	0.9
4	2	9	121.9	125.1	125.1-	2.9
6	2	9	123.8	116.0	116.0-	2.5-
8	2	9	104.0	93.4	93.4-	3.0
10	2	9	91.5	84.1	84.1-	0.6-
12	2	9	67.8	71.1	71.1-	2.5-
1	3	9	89.2	91.7	91.6-	3.9
3	3	9	93.8	89 2	84.7-	28.0
5	3	9	98.8	88.1	87.0-	13.9
7	3	9	93.7	80.3	74.9-	28.9
9	3	9	73.2	61.0	59 7-	12.4
11	3	9	57.1	51.4	51.0-	6.6
0	4	9	38 5	44.0	* 11.3	42.5
2	4	9	38 0	36.0	* 2.7	35 9
4	4	9	36.6	33.9	* 8.9	32.7
6	4	9	35.5	28.2	* 7.8	27.1
8	4	9	32.8	22.8	* 4.4	22.4
10	4	9	20.8	21.9	* 6.2	21.0
1	5	9	89.1	91.8	89 9	18.8
3	5	9	89.3	87.6	87.4	5.6
5	5	9	78.4	78.0	77.5	8.4
7	5	9	92.4	74.3	74.3	0.9
9	5	9	61.0	56.4	56.1	5.5
0	6	9	107.1	111.6	111.6	3.2
2	6	9	94.3	96.8	96.6	6.9-
4	6	9	86.0	92.4	92.3	3.2-
6	6	9	88.3	83.8	83.8	1.8-
1	7	9	45.5	47.0	44.1	16.3-
3	7	9	45.5	45.4	42.3	16.5-
5	7	9	46.3	48.1	42.0	23.5-
0	8	9	14.2	25.2	* 9.7-	23.3-
0	0	10	128.0	148.4	148.3-	4.4-
2	0	10	115.5	120.4	120.3-	3.7
4	0	10	107.4	123.2	123.2-	2.1
6	0	10	108.8	113.8	113.8-	2.7-
8	0	10	89 2	89.4	89.3-	3.7
10	0	10	84.0	83.4	83.4-	0.0-
12	0	10	52 5	64.2	64 2-	1.0-
1	1	10	102.6	94.5	93.7-	12.4
3	1	10	94.8	82 9	81.5-	15.1
5	1	10	94.0	79 1	78.1-	12.5-
7	1	10	72.5	66.7	66.7-	0.6
9	1	10	58.7	55.8	55.8-	0.6
11	1	10	49.4	50.4	50.2-	4.7
0	2	10	37.4	24.2	* 9.3	22.3
2	2	10	37.0	2.1	* 0.4	2.1-
4	2	10	35.5	16.5	* 5.4	15.6
6	2	10	34.3	11.4	* 3.4	10.9
8	2	10	30 5	4.3	* 1.4	4.1
10	2	10	19 3	11.9	* 4.4	11.1
1	3	10	106.6	103.2	103.1	4.8
3	3	10	100.3	90.5	89.7	11.9
5	3	10	98.4	89.3	87.8	16.5
7	3	10	88.9	75.5	72.9	19.5
9	3	10	71.4	62.7	62.2	7.7
11	3	10	49.3	54.7	54.3	6.4
0	4	10	102.7	105.4	105.4	0.9-
2	4	10	99.6	103.3	103.1	5 8-
4	4	10	89.7	93.1	93.0	4.8-
6	4	10	87.8	88.6	88.6	0.7-
8	4	10	76.8	73.7	73.5	4.9-
10	4	10	54 4	61.8	61.8	2.2-
1	5	10	70.9	69.8	66.3	21.9-
3	5	10	66.1	61.1	59.1	15.4-
5	5	10	60.5	57.2	56.3	10.1-
7	5	10	60.9	48.5	48.2	5.7-
9	5	10	37 4	42.3	40.8	11.1-
0	6	10	27.7	23.2	* 8.7-	21.5-
2	6	10	26.3	31.8	* 11.5-	29 6-
4	6	10	22.5	26 3	* 7.8-	25 1-
6	6	10	18.5	26.8	* 7.8-	25.6-
1	7	10	61.9	62.8	61.6-	12.1-
3	7	10	49.4	57.5	56.2-	12.1-
1	1	11	83.1	82.1	81.1	12.6
3	1	11	88.4	82.2	82.2	0.9-
5	1	11	77.4	72.1	72.1	1.6
7	1	11	80.6	71.5	71.4	4.6-
9	1	11	53.6	51.7	51.7	0.2-
0	2	11	95.8	105.2	105.2	2.8-
2	2	11	89.0	96.2	95.8	8.2-
4	2	11	90.8	99.7	99.6	4.6-
6	2	11	93.0	96.1	96.1	0.8
8	2	11	73.1	76.6	76.5	4.1-
10	2	11	59.2	65.0	65.0	1.8-
1	3	11	88.6	78.3	78.3	2.0
3	3	11	76.7	70.2	69.9	6.7-
5	3	11	83.0	73.8	73 3	8.8-
7	3	11	68.9	59.9	59.1	9.6-
9	3	11	51.4	51.8	51.3	7.3-
0	4	11	32.0	20.4	* 4.8-	19.8-
2	4	11	31.1	18.9	* 9.9-	16.1-
4	4	11	28.4	16.1	* 6.1-	14.9-
6	4	11	25.3	14.4	* 6.8-	12.7-
8	4	11	17.5	12.7	* 6.6-	10.9-
1	5	11	89.1	74.1	71.1-	20.9-
3	5	11	73.7	63.3	61.3-	15.9-
5	5	11	76.2	71.3	70 2-	12.3-
7	5	11	48.1	54.1	52.8-	11.6-
0	6	11	67.5	76.4	76.4-	0.6
2	6	11	66.6	76.0	75.8-	4.8
4	6	11	54 1	73.1	73.1-	2.2
0	0	12	100.9	126.9	126.9	3.5
2	0	12	91.0	107.2	107.2	0.8-
4	0	12	85.2	99.0	98.9	4.2-
6	0	12	83.5	86.7	86.7	1.0-
8	0	12	64.5	71.7	71.6	4.1-
1	1	12	72.2	73.1	73.0	3.3-
3	1	12	76.9	69.0	69.0	0.8-
5	1	12	64.1	61.8	61.8	1.7
7	1	12	62.4	57.3	57.1	4.3
9	1	12	38.4	45.6	45 6	1.7-
0	2	12	30 8	5.0	* 2.5-	4.3-
2	2	12	29 9	18.9	* 6.0-	17.9-
4	2	12	27.2	9.3	* 3.3-	8.7-
6	2	12	24.3	11.4	* 3.7-	10.8-
8	2	12	15 5	12.6	* 3.9-	12.0-
1	3	12	84.7	77.6	76.9-	10.2-
3	3	12	72.8	67.6	67.2-	6.9-
5	3	12	74.3	68.5	66.9-	14.7-
7	3	12	58.3	55.6	54.8-	9.4-
0	4	12	86.4	87.5	87.4-	3.6-
2	4	12	87.2	82.8	82.6-	5.6
4	4	12	75 2	71.1	71.0-	3.4
6	4	12	59.2	64.2	64.2-	2.5
1	5	12	58.3	53.3	49.4-	20.1
3	5	12	50 8	49.4	45.0-	20.5
5	5	12	41.1	46.8	45.0-	12.8
1	1	13	76.3	67.8	67.8-	2.6-
3	1	13	68.5	59.8	59.8-	2.0
5	1	13	66.0	63.2	63.1-	3.4-
7	1	13	43.2	50.0	50.0-	0.4
0	2	13	81.6	82.8	82.8-	0.8-
2	2	13	82.6	81.1	81.0-	4.9
4	2	13	76 8	83.3	83.3-	0.3-
6	2	13	70.7	80.6	80.5-	3.6-
1	3	13	59.7	54.8	53.7-	10.8
3	3	13	50.6	52.5	51.5-	10.4
5	3	13	46.1	47.1	45.7-	11.6
0	4	13	18.9	18.2	* 9.8	15.3
2	4	13	17.7	18.7	* 7.9	16.9
4	4	13	12.9	16.5	* 8.1	14.4
0	0	14	72 2	81.1	80.6-	8.9-
2	0	14	70.3	82.6	82.6-	0.2
4	0	14	55.8	67.9	67.9-	1.4-
1	1	14	57.3	52.1	52.1-	1.4
3	1	14	47.7	47.4	47.2-	4.5
0	2	14	17.1	18.1	* 2.4	17.9
2	2	14	15.9	15.1	* 2.6	14.9
4	2	14	10.3	15.7	* 2.4	15.5

* = UNOBSERVED (FO = FMIN)

have been observed had there been no anomalous dispersion. A difference synthesis was then calculated, with coefficients ($F_{obs} \exp 2\pi i\alpha - F_U$), where α is the phase angle calculated for all atoms, and F_U is the contribution of the uranium atom only to the structure factor. The light atoms appeared with peak heights between 7·5 and 11·0 e.Å^{-3}, and no significant detail was apparent. The coordinates thus obtained gave bond lengths which agreed much better with expected values than had those from the least-squares refinement.

Adjustments to the scale factor and uranium temperature parameters were required, and the least-squares refinement then converged satisfactorily. Only in the case of one atom did the final values differ by more than the standard deviation from those obtained from the difference Fourier synthesis. The R index ($\Sigma|\Delta F|/\Sigma|F_o'|$) was 0·101, R' was 0·32, and the parameters thus obtained were considered final. The observed and calculated structure factors are listed in Table 1. Atomic coordinates and temperature factors, together with their standard deviations, are listed in Table 2. The average standard deviation for bond lengths involving the uranium atom is 0·06 Å, and for bond lengths between light atoms 0·09 Å, although the agreement between independent values which on chemical grounds may be assumed equivalent is considerably better than these figures might suggest.

Discussion

The two nitrate ions are coordinated to the uranium atom as bidentate ligands. Two of the water molecules are also coordinated (Fig. 1) and the molecule is thus described as bisnitratodiaquodioxouranium(VI). The coordinated water molecules, the uncoordinated oxygen of the nitrate group and the molecules of water of crystallization are involved in a three-dimensional network of hydrogen bonds, as depicted in Figs. 2–4.

The two U–O bonds of the uranyl group make an angle of 177·3° ($\sigma = 2·5°$) with one another, and angles ranging from 85·8° to 96·2° with the other coordinating bonds. The configuration is thus at least a close approximation to that commonly observed, *i.e.* a linear uranyl group with six atoms coordinated in the plane perpendicular, but it is likely (see below) that some of the apparent deviations from the ideal structure do have meaning.

The uranyl U–O bond lengths are 1·85 and 1·87 Å, somewhat longer than has been predicted from the infrared spectrum (Hoekstra, 1963) although the difference need not be significant. The angles subtended at the uranium atom by the oxygen atoms of the nitrate group, 49·0° and 48·6°, are considerably smaller than is commonly observed between adjacent ligand atoms in coordination compounds, and the ability of uranium to tolerate this small angle is presumably the factor which stabilizes this relatively unusual molecule. The standard deviations do not justify detailed discussion of the nitrate groups, but it may be noted (i) that the deviations from coplanarity (evidenced in Fig. 2) are unlikely to be significant and (ii) that certain features, *viz.* the shorter N–O bond to the non-coordinated oxygen and the smaller angle subtended by the coordinated oxygen atoms at the nitrogen, parallel those previously observed for a bidentate carbonate ion (Barclay & Hoskins, 1962).

The disposition of uranium atoms is necessarily centric, and the immediate environment of each uranium is also very nearly centric. This may be seen from the coordinates in Table 2, it being noted that there exists

Table 2. *Atomic coordinates and temperature parameters*

Coordinates and their standard deviations are expressed as fractions of the cell edge, and thermal parameters and standard deviations in Å^2

Atom	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$B(\sigma_B)$
U	0000(−)	1284(0003)	2500(0018)	—
Uranyl oxygen atoms				
O(1)	0000(−)	0606(0078)	0962(0068)	4·47(1·47)
O(2)	0000(−)	2078(0061)	4035(0054)	3·40(0·72)
Nitrate atoms				
O(3)	0768(0031)	3864(0064)	1783(0040)	4·00(0·53)
N(1)	0000(−)	4737(0078)	1591(0058)	3·01(0·95)
O(4)	0000(−)	6033(0082)	1230(0066)	4·87(1·72)
O(5)	0781(0032)	−1322(0056)	3304(0041)	4·05(0·55)
N(2)	0000(−)	−2270(0071)	3478(0052)	2·54(0·85)
O(6)	0000(−)	−3494(0063)	3960(0059)	3·98(1·12)
Water oxygen atoms				
O(7)	1800(0025)	1287(0042)	2613(0051)	4·25(0·36)
O(8)	2937(0035)	0297(0051)	4270(0052)	4·86(0·88)
O(9)	2930(0030)	2544(0051)	0642(0048)	4·33(0·65)

Values of the uranium temperature parameters in the directions of the principal axes of the vibrational ellipsoid

Axis	B (Å^2)	direction cosines relative to the *abc* axes		
1	3·518	0·0000	0·8349	0·5504
2	2·495	1·0000	0·0000	0·0000
3	1·175	0·0000	−0·5504	0·8349

β_{ij} values ($\times 10^5$)

β_{11}	β_{22}	β_{23}	β_{33}	$(\beta_{12} = \beta_{13} = 0)$
359	1003	527	400	

Table 3. *Environment of the water molecules*

	Atom O(8)		Atom O(9)	
Bond lengths	O(8)–O(9)*a*	2·60 Å	O(9)–O(8)*d*	2·60 Å
	O(8)–O(9)*b*	2·77	O(9)–O(8)*e*	2·77
	O(8)–O(7)	2·55	O(9)–O(7)	2·89
	O(8)–O(6)*c*	2·91	O(9)–O(4)*f*	3·06
Bond angles	O(7)–O(8)–O(9)*a*	89·2°	O(7)–O(9)–O(8)*d*	118·6°
	O(7)–O(8)–O(9)*b*	132·7	O(7)–O(9)–O(8)*e*	99·3
	O(6)–O(8)–O(9)*a*	105·3	O(8)–O(9)–O(8)*e*	101·7
	O(7)–O(8)–O(6)*c*	110·8	O(7)–O(9)–O(4)*f*	98·6
	O(6)–O(8)–O(9)*b*	110·3	O(4)*f*–O(9)–O(8)*e*	78·3
	O(9)*a*–O(8)–O(9)*b*	101·5	O(4)*f*–O(9)–O(8)*d*	142·0

Equivalent positions: $a=\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; $b=x, \bar{y}, \frac{1}{2}+z$; $c=\frac{1}{2}+x, \frac{1}{2}+y, z$; $d=\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{2}+z$; $e=x, \bar{y}, -\frac{1}{2}+z$; $f=\frac{1}{2}+x, -\frac{1}{2}+y, z$; $g=x, 1-y, \frac{1}{2}+z$; $h=x, -1+y, z$.

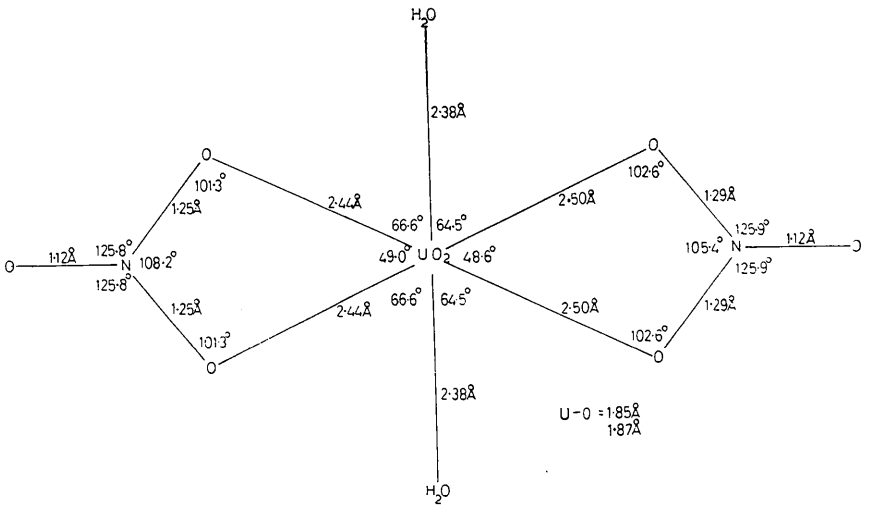

Fig. 1. The coordination about the uranyl group.

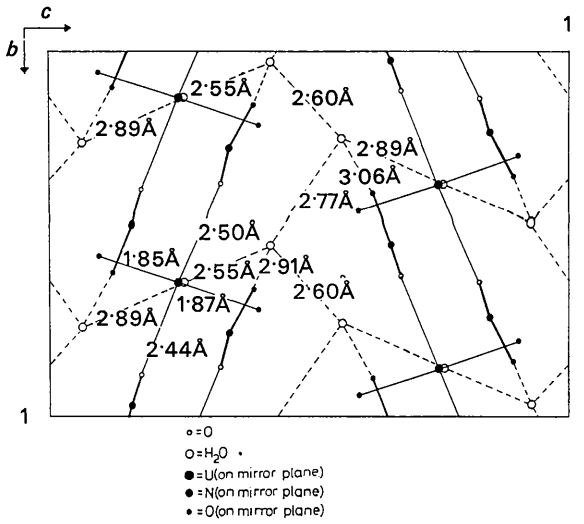

Fig. 2. Projection of the structure on to (100).

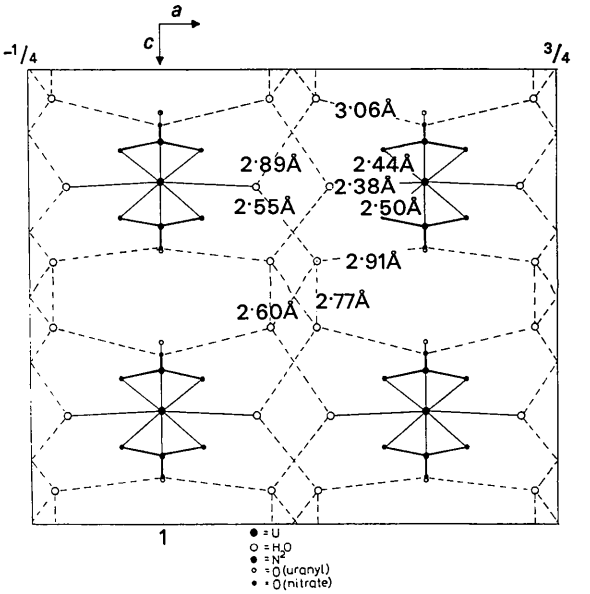

Fig. 3. Projection of the structure on to (010).

a mirror plane in the structure at $x=0$. The y coordinates of water oxygen atoms O(8) and O(9) differ by 0·0273 from centric equivalence about the uranium, but this is the only such difference which is clearly significant. The coordinated water O(7) differs in z from the uranium by 0·0113, *i.e.* by 2σ, with the result that the angle O(7)–U–O(7)′ is 173·7°. Both of the water molecules O(8) and O(9) are involved in hydrogen bonding with O(7), and the result of the above deviations from centricity is that the bond O(8) · · · O(7) (2·55 Å) is considerably shorter than O(9) · · · O(7) (2·89 Å). The details of coordination about O(8) and O(9) are listed in Table 3, and the differences in their environment illustrated in Figs. 2–4. The reason for these minor deviations from a symmetric distribution about the uranium lies presumably in the extra stability arising from the formation of one strong hydrogen bond (*vis-a-vis* two weaker bonds), as there is no other structural cause apparent. The observation of pyroelectricity (Sasvari, 1957) supports the reality of the deviations, as a centric asymmetric unit would not contribute to a pyroelectric vector. The packing of these units is, however, such that the structure as a whole is by no means near-centric, and ferroelectric reversal of the distortion is not at all likely.

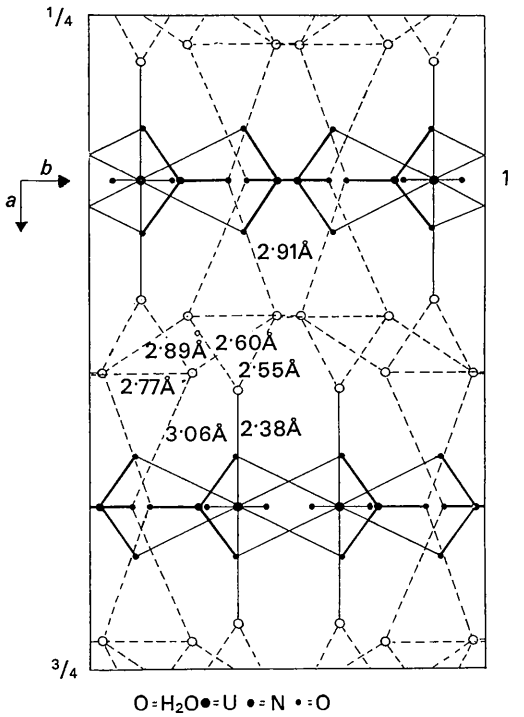

Fig. 4. Projection of the structure on to (001).

It has been concluded from conductivity measurements (Jezowska-Trzebiatowska & Chmielowska, 1961) that the predominant species present in solutions of uranyl nitrate hexahydrate in various organic solvents is the undissociated nitrate associated with four molecules of water, whence it would appear that the preference of the coordinated water molecules for the formation of one strong extramolecular hydrogen bond may not be restricted to the crystalline state.

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References

BARCLAY, G. A. & HOSKINS, B. F. (1962). *J. Chem. Soc.* p. 586.
BOND, W. L. (1959). *Acta Cryst.* **12**, 375.
BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
FLEMING, J. E. & LYNTON, H. (1960). *Chem. and Ind.* p. 1416.
HOEKSTRA, H. R. (1963). *Inorg. Chem.* **2**, 492.
JEZOWSKA-TRZEBIATOWSKA, B. & CHMIELOWSKA, M. (1961). *J. Inorg. Nucl. Chem.* **20**, 106.
MAIN, P. & WOOLFSON, M. M. (1963). *Acta Cryst.* **16**, 731.
PAULING, L. & DICKINSON, R. G. (1924). *J. Amer. Chem. Soc.* **46**, 1615.
ROOF, R. B. (1961). *Acta Cryst.* **14**, 934.
SASVARI, K. (1957). *Acta Geol. Acad. Sci. Hung.* **4**, 3, 467.
THOMAS, L. H., UMEDA, K. & KING, K. (1958). Unpublished work, described by Roof (1961).