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The Crystal Structure of Dicæsium Tetrachlorodioxouranium (VI)

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Dicæsium tetrachlorodioxouranium(VI), $Cs_2UO_2Cl_4$, crystallizes in space group $C2/m$ with 2 molecules in the cell of dimensions $a = 11{\cdot}92$, $b = 7{\cdot}71$, $c = 5{\cdot}83$ Å, $\beta = 99°\ 40'$. The structure contains octahedral $[UO_2Cl_4]^{2-}$ ions, with cæsium ions in elevenfold coordination.

Introduction

Compounds in which uranium(VI) is present as the uranyl group commonly exhibit coordination numbers of 7 and 8, in some cases by the formation of a discrete ion or molecule, *e.g.* $K_3(UO_2F_5)$ (Zachariasen, 1954), and in others by sharing of ligand atoms between uranium atoms, as in $CsUO_2OCl$ (Allpress & Wadsley, 1964). In the latter example both oxygen and chlorine are involved in such sharing, and consequently there appeared some doubt as to the structure of the compound $Cs_2UO_2Cl_4$, which we had recently prepared and had previously assumed to contain an octahedral $[UO_2Cl_4]^{2-}$ ion. In fact this assumption was correct, as has now been proven by determination of the structure.

Experimental

Cæsium uranyl chloride was prepared by adding the stoichiometric quantity of cæsium chloride to a solution of uranyl acetate in dilute hydrochloric acid, and recrystallizing from dilute hydrochloric acid as monoclinic needles elongated along [010].

The b axial length was determined from a calibrated rotation photograph, and a, c and β from Weissenberg photographs. Only one reflexion showed a large α_1–α_2 splitting (007–1·56 mm) and the method of Main & Woolfson (1963) was not applicable. This measurement, together with that of the normal $R\,.\,2\theta$ arc length, did, however, serve to define the film radius precisely. Values of a^* and c^* were obtained from high index $h00$ and $00l$ reflexions, and β from the ratio of diagonals. The cell dimensions were $a = 11{\cdot}92 \pm 0{\cdot}02$, $b = 7{\cdot}71 \pm 0{\cdot}02$, $c = 5{\cdot}83 \pm 0{\cdot}01$ Å, $\beta = 99°\ 40' \pm 20'$. Two molecules per unit cell were assumed on considerations of atomic volumes, leading to a calculated density of 4·261 g.cm^{-3}. Reflexions were systematically absent for hkl when $h+k$ is odd, whence the possible space groups are $C2$, Cm and $C2/m$. The relatively simple structure was found to be consistent with the centrosymmetric space group.

Intensity data for the $h0l$ and $h1l$ layers were collected by visual estimation from Weissenberg photographs. The crystal was approximated to a cylinder, $\mu R = 1{\cdot}53$, and the data corrected for absorption accordingly (Bond, 1959).

Determination of the structure

The uranium atom could unequivocally be positioned at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$ in all space groups. A heavy atom phased electron density projection on (010) (Fig. 1) showed two large peaks in the asymmetric quadrant which could be interpreted as the cæsium and as a double-weight chlorine atom. A rational structure could be envisaged in space group $C2/m$, which was then assumed.

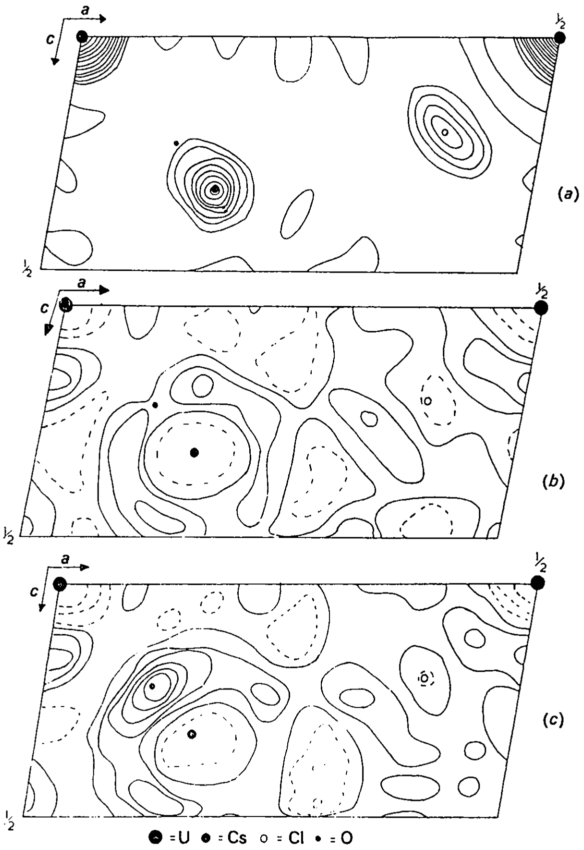

Fig. 1. The (010) projection. (*a*) Initial heavy atom synthesis – contours at arbitrary levels. (*b*) Final difference synthesis. (*c*) Final difference synthesis, with the oxygen atom omitted from F_c-contours at intervals of 2 e.Å^{-2}, dotted lines negative, full lines zero or positive.

Initial refinement was by difference syntheses. The height and curvature of the residual density at the origin were used to establish anisotropic uranium temperature factors and an overall scale constant, using two-dimensional analogues of the equations given by Leung, Marsh & Schomaker (1957), *viz.*

$$D(0) = 2\pi I_1 \Delta k - \frac{\pi}{4} I_3(\Delta B_1+\Delta B_2)\,(1+\Delta k)$$

and

$$\frac{\partial^2 D(0)}{\partial r_i^2} = -4\pi^2 I_3 \Delta k + \frac{\pi^3}{4} I_5(3\Delta B_1+\Delta B_2)\,(1+\Delta k)\,,$$

with the same nomenclature as the above mentioned authors. (The factors $(1+\Delta k)$, which were erroneously omitted from their paper, should be noted.) Assuming this scale constant the residual density at the other atom sites was employed to evaluate isotropic temperature factors. A peak corresponding to the predicted oxygen position was consistently present, and although at this stage variations over the remainder of the map were of almost comparable magnitude the oxygen atom was included in the later cycles. The scattering curves used were those of Thomas, Umeda & King (1958) for uranium, Thomas & Umeda (1957) for positive cæsium ion, Dawson (1960) for chlorine and Freeman (1959) for oxygen. Real dispersion corrections were made of $\Delta f' = -6{\cdot}8$ for uranium (Roof, 1961) and $-1{\cdot}7$ for cæsium (Dauben & Templeton, 1955).

Final refinement was by least squares, using weights determined from the variance in the intensity measurement (Hall, Rae & Waters, 1965). Anomalous dispersion corrections were incorporated ($\Delta f'' = 16{\cdot}0$ for uranium, 8·0 for cæsium) as corrections to the observed amplitudes, *i.e.* $F'_o = (F_o^2 - B^2)^{\frac{1}{2}}$, where $B = \Sigma \Delta f'' \cos 2\pi \mathbf{h}\,.\,\mathbf{r}$. Anisotropic thermal parameters were included for all atoms except oxygen. Omitting four terms which were affected by extinction the R index was 0·095.

The oxygen atom was overlapped in this projection by the cæsium, and a point of interest was then to investigate the ability of these data, visually estimated from non-integrated photographs, to define a single light atom against such a heavy atom background. A final difference synthesis, together with a partial difference synthesis for which the oxygen atom was excluded from F_c, is shown in Fig. 1, and it is apparent that with the other atoms adequately described the residual effect of this oxygen is clearly discernible. The R value increased to 0·128 when the oxygen was omitted.

The only undetermined y parameter, that of the chlorine atom, was assumed on packing grounds to be approximately 0·25. The R value for the $h1l$ data was then 0·116, and a least-squares cycle predicted a

Table 1. *Atom coordinates*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
U	0	—	0	—	0	—
Cs	0·1652	0·0005	0	—	0·3211	0·0011
Cl	0·1016	0·0011	0·2500	0·0098	0·2066	0·0024
O	0·1168	0·0044	0	—	0·2198	0·0101

Table 2. *Observed and calculated structure factors*

H	K	L	FO	FC	
2	0	0	101.4	106.4	
4	0	0	62.2	50.6-	
6	0	0	192.3	190.5	
8	0	0	92.7	83.6	
10	0	0	76.1	75.4	
12	0	0	120.1	112.2	
14	0	0	18.7	18.1	
0	0	1	101.3	115.8	
2	0	1	138.0	128.3	
2-	0	1	158.7	268.1	$
4	0	1	228.5	292.0	$
4-	0	1	22.8	23.9-	
6	0	1	42.4	35.1	
6-	0	1	72.5	69.2	
8	0	1	7.8	13.0	*
8-	0	1	215.2	255.6	
10	0	1	137.3	136.8	
10-	0	1	63.6	58.8	
12	0	1	48.5	56.9	
12-	0	1	9.8	10.9	
14	0	1	28.5	29.5	
14-	0	1	90.4	70.4	
0	0	2	76.4	61.7-	
2	0	2	199.0	279.6	$
2-	0	2	24.2	11.8	*
4	0	2	137.1	142.1	
4-	0	2	222.1	329.5	$
6	0	2	59.2	54.0	
6-	0	2	106.5	110.2	
8	0	2	105.8	118.6	
8-	0	2	60.2	52.0	
10	0	2	26.8	30.5	
10-	0	2	120.7	114.8	
12	0	2	29.4	32.1	
12-	0	2	13.8	16.4	
14-	0	2	53.1	47.7	
0	0	3	155.6	182.1	
2	0	3	44.5	47.1	
2-	0	3	48.5	46.6	
4	0	3	45.6	46.7	
4-	0	3	123.0	143.4	
6	0	3	132.4	167.5	
6-	0	3	184.7	226.8	
8	0	3	51.5	55.6	
8-	0	3	17.6	17.7-	
10	0	3	14.2	18.6	*
10-	0	3	13.9	12.2	
12	0	3	59.5	61.9	
12-	0	3	135.4	135.3	
14-	0	3	53.2	59.8	
0	0	4	99.5	99.8	
2	0	4	10.6	12.5	*
2-	0	4	180.1	224.5	
4	0	4	99.3	112.1	
4-	0	4	24.2	23.5	
6	0	4	52.8	54.5	
6-	0	4	24.4	22.7	
8	0	4	42.7	37.5	
8-	0	4	123.6	127.1	
10	0	4	76.5	72.6	
10-	0	4	44.5	49.5	
12-	0	4	73.4	73.6	
0	0	5	59.5	55.1	
2	0	5	114.0	122.8	
2-	0	5	68.9	73.4	
4	0	5	38.4	40.0	
4-	0	5	111.2	102.3	
6	0	5	14.6	16.2	*
6-	0	5	14.0	5.2-	*
8	0	5	80.6	68.5	
8-	0	5	70.8	78.9	
10-	0	5	153.5	144.7	
12-	0	5	21.4	20.9	
0	0	6	93.0	92.0	
2	0	6	63.4	56.8	
2-	0	6	14.4	7.7	*
4	0	6	31.2	26.4	
4-	0	6	40.4	43.6	
6	0	6	63.0	56.8	
6-	0	6	116.6	112.7	
8-	0	6	45.2	45.3	
10-	0	6	44.5	44.3	
0	0	7	29.2	30.6	
2-	0	7	74.2	61.7	
4-	0	7	30.1	32.0	
6-	0	7	63.8	62.8	
3	1	0	246.7	307.8	$
5	1	0	57.1	44.8	
7	1	0	62.7	50.3	
9	1	0	169.7	177.5	
11	1	0	46.0	43.8	
13	1	0	25.8	25.6	
15	1	0	60.2	68.3	
1	1	1	216.9	319.4	$
1-	1	1	65.2	72.7	
3	1	1	70.8	52.4	
3-	1	1	77.4	82.5	
5	1	1	63.1	46.9	
5-	1	1	200.0	259.8	
7	1	1	193.8	205.9	
7-	1	1	42.0	38.4	
9	1	1	61.4	53.2	
9-	1	1	50.1	49.6	
11	1	1	23.3	25.2	
11-	1	1	134.6	142.4	
13	1	1	83.7	82.3	
13-	1	1	39.7	35.1	
15-	1	1	23.1	24.5	
1	1	2	71.8	59.4	
1-	1	2	185.5	283.1	$
3	1	2	55.2	40.4	
3-	1	2	55.8	57.0	
5	1	2	184.2	217.7	
5-	1	2	76.8	75.7	
7	1	2	67.2	61.9	
7-	1	2	178.2	204.5	
9	1	2	27.7	23.5	
9-	1	2	43.9	32.5	
11	1	2	99.4	93.2	
11-	1	2	48.2	46.0	
13	1	2	39.7	39.7	
13-	1	2	125.0	108.0	
15-	1	2	24.8	27.6	
1	1	3	46.6	33.5	
1-	1	3	68.0	62.9	
3	1	3	183.0	206.8	
3-	1	3	163.2	227.4	
5	1	3	71.1	67.6	
5-	1	3	43.2	44.3	
7	1	3	21.2	21.3	
7-	1	3	70.3	66.3	
9	1	3	104.6	98.2	
9-	1	3	138.9	153.2	
11	1	3	46.1	44.6	
11-	1	3	28.6	27.5	
13-	1	3	41.8	40.3	
1	1	4	163.4	177.6	
1-	1	4	29.0	27.9	
3	1	4	68.6	68.2	
3-	1	4	60.0	61.1	
5	1	4	21.2	19.6	
5-	1	4	140.1	172.7	
7	1	4	100.8	95.9	
7-	1	4	35.5	34.8	
9	1	4	51.4	47.4	
9-	1	4	55.2	56.0	
11	1	4	20.1	22.7	
11-	1	4	120.4	109.8	
13-	1	4	19.0	23.0	
1	1	5	64.6	63.9	
1-	1	5	131.9	141.1	
3	1	5	20.8	18.6	
3-	1	5	20.8	24.0	
5	1	5	97.0	86.8	
5-	1	5	56.2	54.8	
7	1	5	51.8	47.3	
7-	1	5	114.4	125.1	
9	1	5	18.4	22.3	
9-	1	5	26.8	28.2	
11-	1	5	47.0	45.3	
13-	1	5	51.5	75.7	
1	1	6	16.4	17.8	
1-	1	6	57.2	55.9	
3	1	6	89.6	73.2	
3-	1	6	106.6	105.7	
5	1	6	50.8	44.2	
5-	1	6	22.7	21.0	
7-	1	6	51.2	45.9	
9-	1	6	88.5	87.1	
11-	1	6	11.7	22.9	
1	1	7	68.0	58.2	
1-	1	7	14.2	16.6	
3-	1	7	49.0	46.2	
5-	1	7	79.6	75.7	
7-	1	7	11.6	18.2	

* = UNOBSERVED (FO = FMIN)

$ = SECONDARY EXTINCTION.

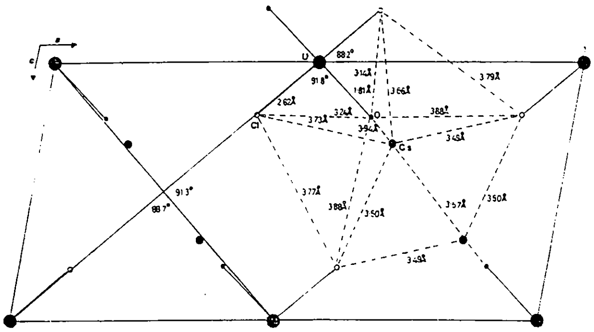

Fig. 2. Interatomic distances and angles.

correction to y_{Cl} of less than one-third its standard deviation. No further refinement was attempted, as the purpose of the investigation had already been achieved.

Atom coordinates, together with their standard deviations, are listed in Table 1. Interatomic distances and angles are shown in Fig. 2. Observed and calculated structure factors are listed in Table 2.

Discussion

Uranium(VI) is six-coordinate in this compound, *i.e.* discrete $[UO_2Cl_4]^{2-}$ ions exist, and no atoms are shared by coordination polyhedra, as occurs with $CsUO_2OCl$. The O–U–O group is linear by symmetry, with the four chlorine atoms in the perpendicular plane. The four U–Cl bonds are necessarily equal, but the chlorine atoms are not at the corners of a square, the angle subtended at the uranium by the mirror related chlorines being 95°. In view of the uncertainty in the chlorine *y* parameter it is doubtful whether this distortion is real.

Eight chlorine and three oxygen atoms at distances between 3·49 and 3·94 Å give the cæsium ion eleven neighbours. The chlorine atoms are arranged approximately at the corners of a cube with the cæsium at the centre (*i.e.* as in cæsium chloride), this cube being somewhat distorted by the three oxygen approaches.

We wish to thank Dr D. van der Helm and Dr A. L. Patterson for making various computer programs available to us, to thank Professor D. R. Llewellyn for his interest in this work, and to acknowledge financial assistance from the Research Committee of the University of New Zealand.

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Isomerism of Benzoquinone Monoximes (Nitrosophenols).
XIII. The Crystal Structure of *p*-Methoxyindophenol *N*-Oxide*

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(*Received* 14 *May* 1965)

The crystals of *p*-methoxyindophenol *N*-oxide are orthorhombic with space group *Pbca* and $Z=8$. The unit-cell dimensions at −180 °C are $a=23{\cdot}91$, $b=12{\cdot}15$, $c=7{\cdot}403$ Å. After several unsuccessful attempts with direct methods the structure was solved from a three-dimensional Patterson analysis with Mo $K\alpha$ data collected at −180 °C.

The anisylic part of the molecule shows the normal distribution of bond distances and bond angles. The benzene ring of this part is tilted, however, by an angle of 64° out of the planar system of the benzoquinone *N*-oxide moiety of the molecule. The distribution of bond angles and bond distances in the latter part is similar to those found in *p*-benzoquinone itself and in *p*-benzoquinone-4-oximes. The bond distances are compared with the results obtained from bond order calculations.

Introduction

The present investigation originated from a spectroscopic study of molecules, free radicals and ions belonging to a class of indophenol dyes. This research was carried out in 1953 by Dr R. Vroom in the department of theoretical organic chemistry, University of Leiden. The compounds studied by Vroom (1966) have the composition

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* Part XII: Romers, 1964.