

1945). The structure of this compound, which is not isostructural with the corresponding calcium and strontium compounds, was discussed in a recent paper

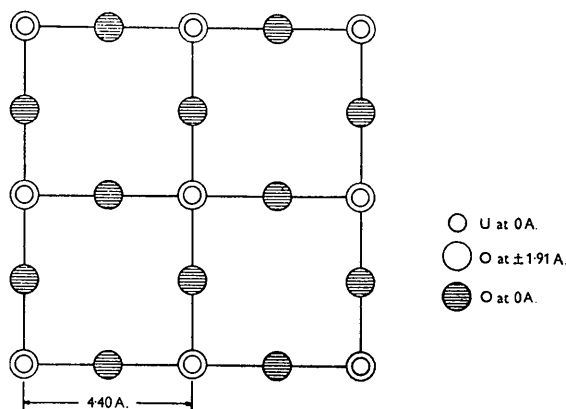


Fig. 3. The tetragonal  $(\text{UO}_2)_2\text{O}_2$  layer which occurs in the structure of  $\text{Ba}(\text{UO}_2)_2\text{O}_2$  proposed by Samson and Sillén.

by Samson & Sillén (1947). These investigators determined the positions of the barium and uranium atoms by means of intensity considerations, and made reasonable guesses as to the location of the oxygen atoms.

The structure proposed for  $\text{Ba}(\text{UO}_2)_2\text{O}_2$  by Samson & Sillén consists of  $(\text{UO}_2)_2\text{O}_2$  layers held by barium atoms situated halfway between the uranium layers. The  $(\text{UO}_2)_2\text{O}_2$  layer in the suggested barium uranate structure is, however, quite different from the one encountered in other uranates. Whereas each uranium atom in  $\text{Ca}(\text{UO}_2)_2\text{O}_2$ ,  $\text{UO}_3$ ,  $\text{UO}_2\text{F}_2$  and in the alkali uranates forms two uranyl bonds and six secondary bonds to other oxygen or fluorine atoms, there are only four of these secondary bonds in barium uranate. The  $(\text{UO}_2)_2\text{O}_2$  layer of barium uranate is shown idealized in Fig. 3.

The writer is indebted to Miss Anne Plettinger who took the X-ray diffraction patterns.

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## Crystal Chemical Studies of the 5f-Series of Elements. V. The Crystal Structure of Uranium Hexachloride

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$\text{UCl}_6$  is hexagonal with three molecules per unit cell. The unit-cell dimensions and the calculated density are:

$$a_1 = 10.95 \pm 0.02 \text{ kX.}, \quad a_2 = 6.03 \pm 0.01 \text{ kX.}, \quad \rho = 3.56 \text{ g.cm.}^{-3}.$$

The space group is  $C\bar{3}m-D_{3d}^3$  and the atomic positions are: 1 U in  $(0, 0, 0)$ , 2 U in  $\pm(\frac{1}{3}, \frac{2}{3}, z)$  with  $z = \frac{1}{2}$ , and three sets of six chlorine atoms in  $\pm(x, 2x, z)$   $(2\bar{x}, \bar{x}, z)$   $(x, \bar{x}, z)$  with parameters as follows:

	$x$	$z$
$\text{Cl}_I$	0.10	0.25
$\text{Cl}_{II}$	0.43	0.25
$\text{Cl}_{III}$	0.77	0.25

The structure is of molecular type. The  $\text{UCl}_6$  molecules are octahedral with  $\text{U-Cl} = 2.42 \pm 0.10 \text{ \AA}$ .

#### Introduction

Uranium forms chlorides  $\text{UCl}_3$ ,  $\text{UCl}_4$ ,  $\text{UCl}_5$  and  $\text{UCl}_6$ . The crystal structures of  $\text{UCl}_3$  (Zachariasen, 1948a) and of  $\text{UCl}_4$  have recently been described. The writer has investigated the structure of  $\text{UCl}_5$  which is monoclinic with four molecules per unit cell. The chlorine positions in the  $\text{UCl}_5$  structure are, however, yet unknown. The present paper discusses the crystal-structure determination of the hexachloride.

A remarkable microsample of uranium chlorides prepared by Dr Sherman Fried was used in the investigation. Within one of the thin-walled glass capillaries used as sample containers for X-ray diffraction specimens on the micro-scale Dr Fried prepared  $\text{UCl}_4$ ,  $\text{UCl}_5$  and  $\text{UCl}_6$ . The three compounds were in three well-separated sublimed zones, green, reddish brown and black in color. Each zone contained only a few micrograms of sublimed material. The black  $\text{UCl}_6$ , being the

most volatile compound of the three, was deposited at the cool end of the capillary, while the red  $\text{UCl}_5$  formed the middle zone. Examination under the microscope showed the black zone to consist of minute crystallites which, however, were too small to yield any information about the crystal form.

The various zones were far enough apart that X-ray diffraction patterns of any one zone could be taken without interference from the other zones. The X-ray diffraction patterns, which were taken with Cu  $K$  radiation filtered through nickel foil, showed the green zone to consist of  $\text{UCl}_4$ , the red zone of  $\text{UCl}_5$ . It was accordingly suspected that the more volatile black material of the third zone would prove to be  $\text{UCl}_6$ .

#### Determination of the structure

The X-ray diffraction data for the black zone are given in Table 1. As indicated in the table, the black zone contained a small amount of  $\text{UO}_2$ . The bulk of the zone is, however, made up of a hexagonal phase with unit-cell dimensions

$$a_1 = 10.95 \pm 0.02 \text{ kX.}, \quad a_3 = 6.03 \pm 0.01 \text{ kX.}$$

Table 1. Powder diffraction data for  $\text{UCl}_6$

$\sin^2 \theta$	$I_{\text{obs.}}$	$H_1 H_2 H_3$
0.0164	Trace	001
0.0198	vs	110
0.0230	s	101
0.0360	w-	111
0.0429	ms	201
0.0596	w+	300 + $\text{UO}_2$ 111
0.0624	m-	211
0.0758	m-	301
0.0791	w	220 + $\text{UO}_2$ 200
0.0850	m-	112
0.1020	w+	311
0.1219	vw	401
0.1245	m	302
0.1384	w	410
0.1414	vw	321
0.1446	w	222
0.1531	vw	103, 411
0.1591	w-	$\text{UO}_2$ 220
0.1730	vw-	203
0.1778	m-	330
0.1811	vw-	501
0.1929	w+	213, 331
0.2037	m- broad	421, 412, 303
0.2191	w+ broad	511 + $\text{UO}_2$ 311

A chlorine atom requires a volume of  $35 \text{ \AA}^3$ . The unit cell given above is thus just big enough to accommodate eighteen chlorine atoms. The fact that all reflections  $H_1 H_2 0$  are absent unless  $H_1 - H_2 = 3n$  requires three uranium atoms per unit cell. The suspicion that the black phase is  $\text{UCl}_6$  is thus confirmed. With three molecules  $\text{UCl}_6$  per unit cell the calculated density becomes  $\rho = 3.56 \text{ g.cm.}^{-3}$ .

It is seen from Table 1 that there are many absent reflections. Most of these absences correspond to reflections  $H_1 H_2 H_3$  for which  $H_3$  is even and  $H_1 - H_2 \neq 3n$ . In order to explain these facts it is necessary to place the three uranium atoms in the positions:  $(0, 0, 0)$ ,  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ ,  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ . These uranium positions account for

the main features of the observed intensity distribution. There are, however, some very serious discrepancies which must be attributed to the chlorine contribution. These discrepancies occur for reflections for which  $H_1$  and  $H_2$  are multiples of three. Hence, one is led to the conclusion that chlorine contributes only to these reflections. The chlorine lattice accordingly corresponds to a hexagonal pseudo-cell with  $a'_1 = \frac{1}{3}a_1$  and  $a'_3 = a_3$ , representing hexagonal close-packing of the chlorine atoms. Indeed, hexagonal close-packing of chlorine atoms with a chlorine radius of 1.81 A. gives for the dimensions of a cell containing eighteen atoms  $a_1 = 10.86 \text{ A.}$  and  $a_3 = 5.91 \text{ A.}$  as against the observed values  $a_1 = 10.95 \text{ kX.}$  and  $a_3 = 6.03 \text{ kX.}$  In order to remove the discrepancies referred to above the close-packed chlorine lattice had to be so adjusted that the uranium atoms fit into 'octahedral' holes. The ideal structure of  $\text{UCl}_6$  obtained in this manner needed a slight distortion corresponding to a small contraction about occupied and a small expansion about vacant 'octahedral' holes.

The final structure arrived at in this way has the space-group symmetry  $C\bar{3}m-D_{3d}^5$ . The atomic positions are: 1 U in  $(0, 0, 0)$ , 2 U in  $\pm(\frac{1}{3}, \frac{2}{3}, z)$  with  $z = \frac{1}{2}$ , 6  $\text{Cl}_I$ , 6  $\text{Cl}_{II}$  and 6  $\text{Cl}_{III}$  in  $\pm(x, 2x, z)$   $(2\bar{x}, \bar{x}, z)$   $(x, \bar{x}, z)$  with parameter values as follows:

	$x$	$z$
$\text{Cl}_I$	$0.10 \pm 0.01$	$0.25 \pm 0.02$
$\text{Cl}_{II}$	$0.43 \pm 0.01$	$0.25 \pm 0.02$
$\text{Cl}_{III}$	$0.77 \pm 0.01$	$0.25 \pm 0.02$

Table 2 shows the comparison between the observed intensities and those calculated on the basis of the structure given above. The simplified intensity formula  $I \propto |F|^2 p$ , where  $p$  is the permutation factor, was used in calculating intensities. Hence, only neighboring reflections should be compared.

Table 2. Observed and calculated intensities

$H_1 H_2 H_3$	$I_{\text{obs.}}$	$I_{\text{calc.}}$	$H_1 H_2 H_3$	$I_{\text{obs.}}$	$I_{\text{calc.}}$
100	Nil	0	410	w	9.9
001	Trace	0.3	321	vw	8.8
110	vs	6.8	222	w	9.9
101	s	5.9	003	Nil	0.2
200	Nil	0	312	Nil	0
111	w-	1.4	103	vw	{4.3
201	ms	5.4	411		{2.1
210	Nil	0	500	Nil	0
300	w+*	1.5	113	Nil	1.0
211	m-	10.3	402	Nil	0
002	Nil	0	203	vw-	4.1
102	Nil	0	330	m-	15.4
301	m-	8.2	501	vw-	4.0
220	w*	5.5	420	Nil	0
112	m-	11.0	322	Nil	0
310	-	0	213		{7.9
202	Nil	0	331	w+	{1.0
221	Nil	1.2	421		{7.6
311	w+	9.4	412		{17.2
400	Nil	0	510	m-	{0
212	Nil	0	303		{5.8
401	vw	4.5	511	w+*	7.4
302	m	21.0			
320	-	0			

\* Coincidence with  $\text{UO}_2$  reflection.

### Discussion of the structure

A projection of the structure seen along the sixfold axis is shown in Fig. 1. The slightly distorted hexagonal close-packing of the chlorine atoms is immediately apparent.

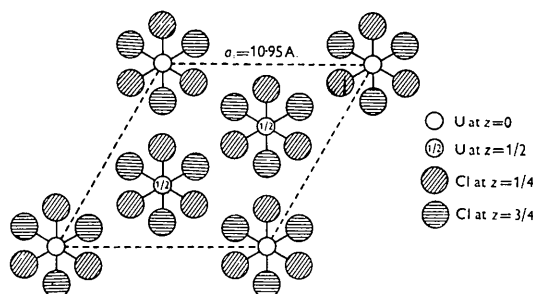


Fig. 1. The  $\text{UCl}_6$  structure viewed along the sixfold axis. The U-Cl bonds within the  $\text{UCl}_6$  molecules are indicated.

Fig. 1 clearly shows that  $\text{UCl}_6$  has a typical molecular structure, being built up of individual molecules  $\text{UCl}_6$  in a three-dimensional array. The structure thus provides a direct explanation of the observed high volatility of the substance.

The six chlorine atoms about each uranium atom

form a nearly perfect octahedron. The U-Cl distance is 2.42 Å. This distance is probably accurate to only  $\pm 0.1$  Å., since it was difficult to determine the chlorine parameters with accuracy from the powder diffraction data. The normal single-bond radius of chlorine being 0.99 Å., one finds the value 1.43 Å. for the single-bond radius of hexavalent uranium. In the preceding paper of this series (Zachariasen, 1948*b*) essentially the same single-bond radius for uranium was deduced. The metallic single-bond radius is according to Pauling (1947) for comparison 1.42 Å. This agreement represents further support for the contention of V. M. Goldschmidt and of Pauling that covalent and metallic radii are essentially the same.

The closest distance between chlorine atoms of different  $\text{UCl}_6$  molecules is 3.85 Å.

The writer thanks Dr Sherman Fried for the  $\text{UCl}_6$  preparation and Miss Anne Plettinger for having taken the diffraction patterns.

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## The Crystal Structure of Zirconium Oxysulfide, $\text{ZrOS}^*$

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The crystal structure of  $\text{ZrOS}$  has been investigated by means of X-ray powder photographs and by powder spectrometry. The substance has a simple cubic lattice with  $a_0 = 5.696 \pm 0.002$  Å. ( $\lambda = 1.5418$  Å.) with space group  $T^4-P2_13$ . In the resulting structure Zr shows a co-ordination number of seven, being surrounded by three sulfur atoms at 2.63 Å., one sulfur atom at 2.61 Å. and three oxygen atoms at 2.13 Å. The co-ordination polyhedron has a point-group symmetry of  $C_{3v}-3m$ .

### Introduction

When  $\text{H}_2\text{S}$  gas was passed through a graphite tube containing  $\text{ZrO}_2$  at  $1300^\circ\text{C}$ . a product which showed gradation in color from pale yellow to a dark purple resulted. The material was divided into five portions according to color, and X-ray powder patterns were photographed for the three samples corresponding to greatest interaction with  $\text{H}_2\text{S}$ . The darkest sample (no. 5) proved to be  $\text{ZrS}_2$ , for which cell constants of

$a = 3.66$  Å. and  $c = 5.79$  Å. ( $\lambda = 1.542$  Å.) were found. Sample no. 3, a yellow powder, was found to be  $\text{ZrOS}$  with a few of the stronger lines of  $\text{ZrO}_2$  appearing. The diffraction pattern of sample no. 4 showed lines of both  $\text{ZrOS}$  and  $\text{ZrS}_2$ , the  $\text{ZrOS}$  phase having the same cell constant as in sample no. 3, where there was a slight excess of  $\text{ZrO}_2$ . This latter observation indicates that neither  $\text{ZrO}_2$  nor  $\text{ZrS}_2$  are highly soluble in  $\text{ZrOS}$ , since a shift in cell constant would be expected in that case. However, our cell constants for  $\text{ZrS}_2$ , which are lower than those reported in the literature (van Arkel, 1924; *Strukturbericht*, 1931), indicate that there may be some unreplaced oxygen in that phase.

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