

Precision Determination of the Crystal Structure of Osmium Dioxide

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The crystal structure of osmium dioxide has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques down to a final R -value of 0.031 on F . It is confirmed that OsO_2 has a rutile structure. The material crystallizes in space-group $P4_2/mnm$ of the tetragonal system with two formula units in the unit cell. The dimensions of the unit cell have been determined from powder photographs taken with a Guinier camera and found to be $a=4.500$, Å, $c=3.183$, Å, and $V=64.48$ Å³. The structural parameter has been determined by the use of three-dimensional X-ray data and found to be 0.308 ± 0.002 . Osmium is octahedrally coordinated by oxygen, four of the six Os—O distances being 2.006 ± 0.008 Å and the other two somewhat shorter, *viz.* 1.962 ± 0.013 Å. This small difference, the same as for RuO_2 , is significant according to the Cruickshank test. The shortest Os—Os distance is 3.184 Å thus excluding appreciable metal-metal interaction.

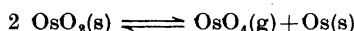
Goldschmidt¹ reported in 1926 that osmium dioxide has a rutile structure like RuO_2 . Since the present author has recently studied the structure of RuO_2 ¹¹ it seemed appropriate to refine the structure of OsO_2 too. This was done chiefly on the same grounds as for RuO_2 . No recent investigation with modern X-ray technique had been made, and the earlier work was based on powder diffraction methods.

Two sets of Weissenberg photographs were taken, one along the a -axis ($0kl-6kl$) and one along the c -axis ($hk0-hk4$), but in the meantime a diffractometer became available at the Department of Inorganic Chemistry, University of Göteborg, and thus a precision determination of the crystal structure of OsO_2 could be made.

EXPERIMENTAL

It proved to be rather difficult to obtain single crystals of OsO_2 . Several methods²⁻⁴ were tried to prepare the crystalline material without success. Wöhler and Metz's method⁵ was also tried; it involves the passage of NO through a silica tube containing osmium

powder in a small silica boat, the tube being heated to 550°C in a furnace. But the osmium powder I had at my disposal was probably too finely divided since no OsO₂ crystals were formed. The method described by Ruff and Rathsburg,⁶ in principle consisting of heating osmium powder in osmium tetroxide vapours to 650°C, was tried but with negligible yield. Eventually it turned out that the simplest way to prepare crystals of OsO₂ was as follows: a silica tube, about 15 cm long, and containing a small amount (0.1–0.3 g) of black amorphous OsO₂, was sealed at both ends. The amorphous OsO₂ used in the preparation was obtained by reduction of an aqueous solution of OsO₄ with ethanol. The black precipitate formed was then filtered off, washed, and dried at 100°C. The amorphous dioxide was collected at one end of the silica tube, and this end was placed in a furnace and heated to 800–1000°C for 10–20 h. The end projecting out from the furnace was maintained at room temperature. At temperatures above 500°C, OsO₂ decomposes reversibly according to the formula:



This reaction proceeds appreciably to the right at 800–1000°C, and the OsO₄ so formed in the warmer part of the tube decomposes again in the cooler part forming crystals of OsO₂. After the heating the tube was opened and a minute quantity of gold glittering, yellowish brown crystals was found in that part of the tube which had been outside the furnace.

CELL DIMENSIONS

The cell dimensions of osmium dioxide were determined by means of a Guinier camera using CuKα₁ radiation with λ=1.54050 Å and with KCl as internal standard (a_{KCl}=6.2919₄ Å at 20°C).⁷ Twelve reflections were measured. These were indexed and the cell constants were calculated using the programme POWDER⁸ and the computer IBM 360/50 at Göteborgs Data-central. The following results were obtained.

$$\begin{aligned} a &= 4.5003 \pm 0.0005 \text{ \AA} \\ c &= 3.1839 \pm 0.0004 \text{ \AA} \\ c:a &= 0.7075 \\ V &= 64.48 \text{ \AA}^3 \end{aligned}$$

These values are in good agreement with those published by Goldschmidt,¹ viz. $a=4.51 \pm 0.02$ Å, $c=3.19 \pm 0.02$ Å and $c:a=0.707$. The density calculated from these dimensions with two formula units in the unit cell is 11.44 g/cm³

Table 1. Guinier powder photograph of OsO₂, CuKα₁ radiation (λ=1.54050 Å).

<i>h k l</i>	10 ⁵ sin ² θ obs	10 ⁵ sin ² θ calc	<i>I</i> obs	<i>F</i> calc
1 1 0	5861	5859	vs	139
1 0 1	8780	8782	vs	122
2 0 0	11721	11717	s	110
2 1 1	20501	20499	w	120
0 0 2	23413	23411	vs	129
2 2 0	23442	23435	s	122
1 1 2	29292	29269	s	110
3 1 0	29292	29294	s	104
3 0 1	32222	32217	m	117
2 0 2	35120	35128	s	94
3 2 1	43943	43934	m	91
2 2 2	46841	46845	m	103

in good agreement with the experimental value 11.38 g/cm³ given by Krauss and Schrader.¹⁷ A comparison between observed and calculated sin² θ values is shown in Table 1.

COLLECTION OF DIFFRACTION DATA AND DATA CORRECTION

As in the case of RuO₂¹¹ it was difficult to find a single crystal of osmium dioxide since most crystals were twinned. Many crystals had to be tested on the goniometer before a suitable specimen was found. The chosen crystal, which measured 0.063 mm along the *c*-axis and had a cross-section of 0.019 × 0.020 mm, was mounted on a glass fibre about the *c*-axis, and the intensity data were collected using a Philips Pailred automatic, single crystal X-ray diffractometer. MoK α radiation was employed and 484 reflections were measured, of which 145 were independent. Errors in the intensity data due to absorption could not be neglected since the calculated value⁹ of the linear absorption coefficient is as high as 1040 cm⁻¹.

The data obtained were transferred to the computer IBM 360/50 at Göteborgs Datacentral. Transformation and correction for absorption, Lorentz' and polarization effects were performed by the programme DATAP2,¹⁰ modified by Ove Lindgren for use at the Department of Inorganic Chemistry, University of Göteborg.

REFINEMENT OF THE STRUCTURE

The indices of the reflections showed the same systematic absences as found for RuO₂.¹¹ Thus the refinement was started in space-group *P*4₂/*mnm* (No. 136)¹² with osmium in 2(*a*): 0,0,0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and oxygen in 4(*f*): *x, x, 0*; $\bar{x}, \bar{x}, 0$; $\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}$; $\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}$. This resulted finally in an *R*-value of 0.031, and the other two space-groups possible were not tried. As a starting value for the parameter *x*, the value 0.306 obtained for RuO₂¹¹ was used. Initially all the 484 reflections recorded were used in a refinement of atomic coordinates and isotropic temperature factors, the programme LALS¹⁰ being employed. Atomic scattering factors for the neutral atoms were taken from Cromer and Waber¹³ and each structure factor was weighted according to Hughes.¹⁴ After five cycles the *R*-value was 0.065. Mean values of the equivalent reflections

Table 2. Anisotropic temperature factors. The first row shows the values obtained for all the 145 reflections and the second row the values when eleven among the strongest reflections were omitted. The anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os	-0.0001	-0.0001	0.0012	0.0000	0.0000	0.0000
O	-0.0010	-0.0010	0.0359	-0.0027	0.0000	0.0000
Os	0.0007	0.0007	0.0027	0.0000	0.0000	0.0000
O	0.0003	0.0003	0.0331	-0.0021	0.0000	0.0000

were now calculated and the refinement was continued with the resulting 145 independent reflections. The R -value decreased to 0.046 with isotropic temperature factors and to 0.043 when anisotropic temperature factors were introduced. The anisotropic temperature factors, however, were very low or even negative as can be seen in the first row of Table 2. Eleven among the strongest reflections, which were most strongly affected by secondary extinction, were then omitted. The new anisotropic temperature factors obtained seemed more realistic, see Table 2, the second row. The R -value decreased to 0.031, but the atomic parameters did not change appreciably.

The atomic parameters are given in Table 3, which shows the values obtained before and after introducing anisotropic temperature factors. The

Table 3. Atomic parameters before and after introducing anisotropic temperature factors. (Estimated standard deviations in parentheses.)

	x	y	z	B
Os	0	0	0	0.01(1) Å ²
O	0.3079(29)	0.3079(29)	0	0.35(15) Å ²
Os	0	0	0	
O	0.3081(20)	0.3081(20)	0	

values obtained when eleven of the strongest reflections were excluded on account of secondary extinction, were the same as those in the second row. The final value for the oxygen parameter is thus 0.308 ± 0.002 . A comparison between the observed and calculated structure factors for the 134 reflections is given in Table 4.

The results were checked by calculating three-dimensional Fourier and difference Fourier maps using the programme DRF.¹⁰ No discrepancies were found; the highest peaks in the latter map were less than 1 % of the highest peaks in the former.

Interatomic distances and angles together with their standard deviations were calculated with the programme DISTAN.¹⁰ The essential values are listed in Table 5.

DISCUSSION

The rutile structure of osmium dioxide is confirmed, and the long Os—Os distances prove that there are no metal-metal bonds present. As in the RuO₂¹¹ case the metal atom is octahedrally coordinated by oxygen with two Os—O distances somewhat shorter than the rest, the difference being only 2 %, but significant according to Cruickshank.¹⁵ The deviations in bond length are the same for RuO₂ and OsO₂, both having two shorter and four longer bonds, as compared with rutile (TiO₂) which according to Baur¹⁶ has four shorter and two longer bonds also differing with 2 %.

Table 4. Observed and calculated structure factors for OsO₂.

H	Y	L	F _o	F _c	H	Y	L	F _o	F _c	H	Y	L	F _o	F _c	H	Y	L	F _o	F _c
0	2	6	49	49	1	2	7	45	42	2	2	6	49	50	3	3	4	66	66
0	4	6	46	47	1	1	6	53	51	2	4	6	46	45	3	5	4	53	53
0	1	5	63	61	1	3	6	49	48	2	3	5	53	55	3	7	4	47	49
0	3	5	63	61	1	5	6	48	45	2	5	5	50	52	3	4	3	69	69
0	5	5	50	49	1	2	5	59	61	2	7	5	42	43	3	6	3	63	60
0	7	5	50	46	1	4	5	57	55	2	2	4	68	72	3	8	3	44	44
0	0	4	82	80	1	6	5	47	47	2	4	4	63	62	3	3	2	82	88
0	2	4	69	69	1	1	4	72	75	2	6	4	51	52	3	5	2	67	64
0	4	4	65	65	1	3	4	66	67	2	8	4	47	47	3	7	2	62	59
0	6	4	61	57	1	5	4	61	61	2	3	3	69	73	3	9	2	46	46
0	8	4	44	43	1	7	4	50	49	2	5	3	67	69	3	4	1	82	83
0	1	3	85	88	1	2	3	82	87	2	7	3	54	53	3	6	1	71	70
0	3	3	84	87	1	4	3	73	74	2	9	3	43	44	3	8	1	51	49
0	5	3	62	63	1	6	3	64	61	2	4	2	77	80	3	3	0	99	101
0	7	3	58	58	1	8	3	51	51	2	6	2	63	63	3	5	0	72	69
0	9	3	46	46	1	5	2	77	78	2	8	2	56	56	3	7	0	67	64
0	4	2	84	86	1	7	2	59	59	2	5	1	84	84	3	9	0	50	49
0	6	2	68	71	1	9	2	46	48	2	7	1	61	60	4	4	6	42	43
0	8	2	49	49	1	4	1	88	91	2	9	1	48	49	4	5	5	44	46
0	5	1	76	74	1	6	1	69	70	2	4	0	89	89	4	4	4	56	56
0	7	1	71	68	1	8	1	60	59	2	6	0	71	68	4	6	4	52	50
0	9	1	51	51	1	10	1	44	43	2	8	0	62	60	4	5	3	60	59
0	2	0	104	110	1	3	0	98	103	2	10	0	39	42	4	7	3	51	50
0	4	0	96	97	1	5	0	87	86	3	3	6	48	47	4	4	2	69	71
0	6	0	82	78	1	6	0	7	6	3	5	6	41	41	4	6	2	63	60
0	8	0	55	52	1	7	0	65	64	3	4	5	50	52	4	8	2	48	48
0	10	0	48	50	1	9	0	54	51	3	6	5	47	47	4	5	1	71	68

Table 5. Distances and angles. (Estimated standard deviations in parentheses.)

(Os—O) ₁	(2 ×)	1.962(13) Å
(Os—O) ₂	(4 ×)	2.006(8)
(Os—Os) _{1=c}	(2 ×)	3.1839(4)
(Os—Os) ₂	(8 ×)	3.5582(6)
(O—O) ₁	(2 ×)	2.441(20)
(O—O) ₂	(8 ×)	2.806(13)
(O—O) _{3=c}	(2 ×)	3.1839(4)
(O—Os—O) ₁		75.0(0.5)°
(O—Os—O) ₂		90.0(0.1)
(O—Os—O) ₃		105.0(0.5)

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