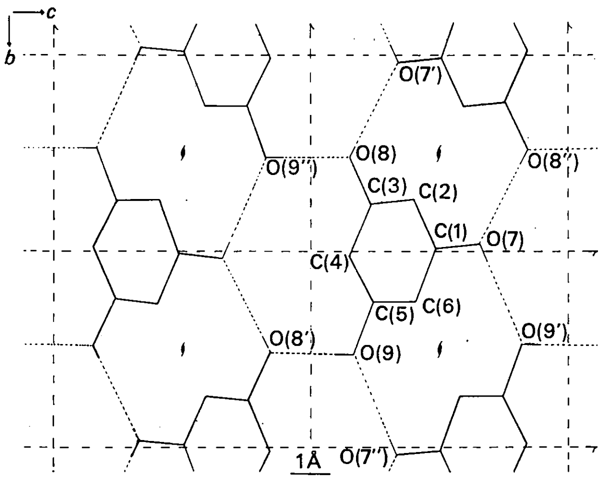

Fig. 2. Arrangement of molecules viewed down the a-axis. Broken lines indicate hydrogen bonds. O(7′) belonges to a molecule one repeat distance above the molecule of O(8″). Similarly O(7″) belongs to a molecule one repeat distance above the molecule of O(9′).

ing line between neighbouring oxygen atoms then in accordance with the valency angle of oxygen the donor-acceptor direction in the helices is likely to be as indicated in Fig. 2.

As mentioned above, the three oxygen atoms of the molecule are all found on the same side of the plane of the benzene ring. This may be related to the situation that the six neighbouring oxygen atoms to which these three are linked by hydrogen bonding are also found on this same side of the plane. As there are no short intermolecular distances in the direction normal to the plane of the benzene ring, the non-planarity of the molecule as a whole (considering carbon and oxygen atoms only), may be due to internal conditions rather than to external ones.

An analysis of the parameters describing the anisotropic thermal motion shows that the largest axes of the vibrational ellipsoids are roughly perpendicular to the plane of the molecule.

On request, a list of structure amplitudes is available from the author.

The author is most indebted to Prof. Dr J. A. Goedkoop and Dr B. O. Loopstra for their interest in this work and for many valuable discussions. The assistance received from the computer staff at this institute is gratefully acknowledged.

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The Crystal Structure of Osmium Tetroxide

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Crystals of OsO_4 are monoclinic, space group $C2/c$, with 4 molecules in the cell with dimensions

$a=9{\cdot}379$, $b=4{\cdot}515$, $c=8{\cdot}632$ Å; $\beta=116{\cdot}6°$.

By least-squares refinement of three-dimensional X-ray diffraction data the molecules are tetrahedral with Os–O = 1·74 Å (uncorrected for thermal motion). The molecular arrangement is approximately cubic closest packing. The intermolecular O–O distances exceed 2·98 Å and are consistent with weak intermolecular forces indicated by the high vapor pressure and low melting point.

Introduction

The crystal structure of osmium tetroxide was investigated previously by X-ray photographic methods (Zalkin & Templeton, 1953), but oxygen positions were not determined from the intensity data. The complete structure has now been established with intensity data from the direct counting technique. The new study shows that the old unit cell must be doubled and that the wrong space group had been chosen.

Experimental

Crystals of OsO_4 were grown in sealed glass capillaries by sublimation at room temperature. Raw crystals were obtained from A. D. Mackay, Inc. Rotation, oscillation and Weissenberg photographs were taken using Cu radiation with Ni filter. A crystal with dimensions $0.19 \times 0.063 \times 0.092$ mm was mounted on a goniostat on a General Electric XRD 5 apparatus equipped with a scintillation counter and pulse height discriminator. Accurate cell dimensions were determined using the goniostat and Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å). Intensities were measured for each independent reflection with $\sin\theta/\lambda$ less than 0·71 ($2\theta < 60°$) with 10 seconds counting time for each reflection. A total of 479 independent reflections were measured exclusive of space group extinctions. The linear absorption coefficient is estimated to be $\mu = 394$ cm^{-1} for Mo $K\alpha$ radiation, and the absorption effect is appreciable. Absorption corrections were made after partial refinement of the structure, as described later. No correction was made for extinction.

Calculations were made with an IBM 7090 computer using our version of the Gantzel–Sparks–Trueblood full-matrix least-squares program (unpublished). The function minimized was

$$\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2 ,$$

with unit weight assigned to each of the 479 reflections.

The atomic scattering factors for neutral O and Os were taken from Ibers (1962).

Crystal data

The crystals are colorless, with a low melting point (about 40°C) and high vapor pressure (Ogawa, 1931). They are monoclinic, with

$$a = 9.379 \pm 0.005 \text{ Å } (9.39 \text{ Å}),$$
$$b = 4.515 \pm 0.002 \text{ Å } (4.52 \text{ Å}),$$
$$c = 8.632 \pm 0.003 \text{ Å } (8.66 \text{ Å}),$$
$$\beta = 116.6° \pm 0.05° \ (116.7°),$$
$$V = 330.7 \text{ Å}^3.$$

The values in parentheses are from Zalkin & Templeton (1953), changed to the new setting. With $Z = 4$ the calculated density is 5·10 g.cm^{-3}, compared with 4·95 observed by Krauss & Schrader (1928). The systematic absences:

$$hkl \text{ absent if } h+k \neq 2n;$$
$$h0l \text{ absent if } h \neq 2n \text{ or if } l \neq 2n$$

are characteristic of space groups Cc and $C2/c$. The centrosymmetric group, $C2/c$, was chosen, and later it was confirmed by the successful result of the structure determination. Reflections are strong if $h+k=2n$ and $h+l=2n$; otherwise they are weak or absent. If these weak reflections were all absent, the lattice would be face-centered, and a smaller C-centered cell could be chosen. In the previous study (Zalkin & Templeton, 1953) these weak reflections escaped notice, and the lattice was described on the smaller cell.

Determination of the structure

The osmium atoms must conform closely to a face-centered structure to explain the strong reflections. In space group $C2/c$ this is possible with special positions 4(c), 4(d), and 4(e). Since we expected OsO_4 to be tetrahedral, the sets (c) and (d), at centers of inversion, were discarded, and the set 4(e):

$$(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, 0) \pm (0, y, \tfrac{1}{4})$$

was chosen with y approximately 0·25.

This structure for the osmium atoms explains the largest peaks in the Patterson function. On the basis of smaller peaks in the Patterson function and expected molecular dimensions, two sets of oxygen atoms were placed in general positions 8(f):

$$(0, 0, 0; \tfrac{1}{2}, \tfrac{1}{2}, 0) \pm (x, y, z; x, -y, \tfrac{1}{2}+z)$$

with coordinates (0·12, 0·05, 0·19) and (0·12, 0·45, 0·43). This trial structure was refined by least squares. With isotropic temperature factors of the form $\exp(-B\lambda^{-2}\sin^2\theta)$ and no correction for absorption, the discrepancy index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was reduced to 0·170.

At this stage the discrepancies between the observed and calculated structure factors were fairly large; therefore some of the intensities were remeasured. Another series of least-square refinement reduced R to 0·165. Inspection of the structure factors then revealed a systematic discrepancy which we attribute to absorption errors. In general, $|F_o|$ exceeded $|F_c|$ for negative l and $|F_o|$ was less than $|F_c|$ for positive l. The intensities were measured with φ less than or more than 33° for these two classes of reflections, respectively. Measurements of 020 and 040 as a function of φ (the spindle axis of the goniostat) in the full circular range showed that their intensities varied in a manner that could be approximated by a sinusoidal curve. The

Table 1. *Final coordinates and estimated standard deviations*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Os	0	0·2601	$\frac{1}{4}$	—	0·0004	—
O(1)	0·121	0·038	0·190	0·003	0·007	0·004
O(2)	0·115	0·476	0·425	0·003	0·006	0·003

Table 2. *Final thermal parameters and estimated standard deviations**

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os	1·47	1·96	1·84	0	0·54	0
O(1)	4·0	4·2	5·1	0·9	3·1	0·2
O(2)	3·8	3·8	2·9	−0·9	0·4	−1·2

Atom	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Os	0·05	0·06	0·06	—	0·04	—
O(1)	1·1	1·3	1·3	1·0	1·1	1·1
O(2)	1·1	1·2	1·0	1·0	0·8	0·9

* $4\beta_{ij} = b_i b_j B_{ij}$, where b_i is the length of the ith reciprocal axis.

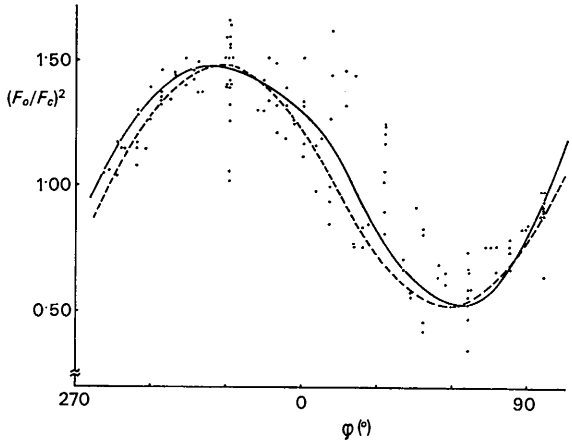

Fig. 1. Ratio of observed to calculated intensity as a function of φ. The solid curve is the ratio for 020, which can be measured at any φ because χ is 90°. The broken curve corresponds to the correction equation.

ratios of observed to calculated intensities for strong reflections, when arranged as a function of φ, tend to follow a similar variation (Fig. 1). While the absorption effect cannot be a function simply of φ, it obviously has a strong correlation with this variable. The intensities were corrected with the empirical relation:

$$|F_o|^2(\text{corrected}) = |F_o|^2[1+0{\cdot}45\cos(2\varphi+64°)]^{-1}.$$

After this correction, refinement reduced R to 0·107.

With an anisotropic temperature factor of the form $\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-2\beta_{13}hl)$ for the osmium atom, R was reduced to 0·082. The final series of refinement was carried out with similar anisotropic temperature factors (except that all three cross terms are included) for the oxygen atoms. The final $R=0{\cdot}082$ was no better, the sum of squares of residuals decreased only slightly, and the deviations from isotropy of the oxygen atoms hardly exceed the standard deviations.

Table 3. *Observed structure factor magnitudes* (FOB) *and calculated strcuture factors* (FCA), *each multiplied by* 10

H,K= 0, 0

L	FOB	FCA
2	234	-274
4	196	199
6	163	-159
8	93	93
10	61	-67

H,K= 2, 0

L	FOB	FCA
-10	72	-74
-8	122	118
-6	161	-157
-4	163	152
-2	226	-268
0	293	283
2	201	-223
4	212	216
6	138	-133
8	80	85

H,K= 4, 0

L	FOB	FCA
-10	86	-83
-8	139	133
-6	160	-157
-4	197	200
-2	222	-224
0	201	158
2	189	-183
4	160	153
6	104	-100
8	73	77

H,K= 6, 0

L	FOB	FCA
-12	41	49
-10	84	-79
-8	116	111
-6	163	-151
-4	209	210
-2	212	-186
0	199	163
2	161	-150
4	99	102
6	74	-80

H,K= 8, 0

L	FOB	FCA
-10	67	-68
-8	92	85
-6	125	-120
-4	142	142
-2	162	-141
0	172	143
2	121	-109
4	77	80

H,K=10, 0

L	FOB	FCA
-10	59	-62
-8	73	78
-6	89	-91
-4	90	93
-2	116	-102
0	104	96
2	80	-76

H,K=12, 0

L	FOB	FCA
-8	62	68
-6	62	-73
-4	64	74
-2	68	-73

H,K= 1, 1

L	FOB	FCA
-11	52	-57
-10	4	2
-9	83	86
-8	12	-9
-7	131	-126
-6	37	36
-5	181	174
-4	11	-5
-3	213	-220
-2	21	18
-1	239	278
0	23	-19
1	206	-263
2	72	-60
3	206	215
4	0	-7
5	167	-163
6	16	15
7	112	111
8	0	-1
9	69	-77
10	5	7

H,K= 3, 1

L	FOB	FCA
-11	57	-62
-10	5	-1
-9	97	94
-8	9	-11
-7	146	-136
-6	7	8
-5	179	174
-4	30	-19
-3	213	-214
-2	105	90
-1	208	230
0	21	-17
1	174	-210
2	10	2
3	186	182
4	16	-18
5	142	-134
6	4	-5
7	93	95
8	11	-3
9	57	-64

H,K= 5, 1

L	FOB	FCA
-11	62	-62
-10	10	6
-9	100	94
-8	7	-3
-7	136	-131
-6	19	-17
-5	177	168
-4	27	-12
-3	198	-195
-2	27	20
-1	169	188
0	13	-9
1	156	-171
2	36	35
3	142	140
4	16	-10
5	104	-104
6	0	1
7	72	76

H,K= 7, 1

L	FOB	FCA
-11	58	-60
-10	14	11
-9	89	85
-8	5	-6
-7	114	-113
-6	8	5
-5	151	142
-4	15	-5
-3	154	-155
-2	35	-16
-1	143	152
0	11	-7
1	131	-135
2	13	14
3	101	106
4	0	-2
5	79	-81
6	6	8

H,K= 9, 1

L	FOB	FCA
-11	54	-55
-10	5	5
-9	76	74
-8	11	-10
-7	93	-94
-6	11	19
-5	108	109
-4	5	-9
-3	103	-115
-2	11	3
-1	105	113
0	8	-8
1	93	-98
2	0	-0
3	73	79
4	17	-3

H,K=11, 1

L	FOB	FCA
-10	0	-1
-9	56	62
-8	6	-4
-7	68	-76
-6	8	8
-5	73	83
-4	10	-8
-3	73	-85
-2	11	11
-1	70	80
0	5	-6
1	58	-69

H,K=13, 1

L	FCB	FCA
-5	49	62

H,K= 0, 2

L	FCB	FCA
0	174	-157
10	56	61
1	16	17
2	198	203
3	12	-13
4	181	-174
5	25	25
6	124	121
7	16	-14
8	92	-97
9	12	10

H,K= 2, 2

L	FCB	FCA
-10	67	69
-9	5	-8
-8	100	-95
-7	22	19
-6	152	139
-5	31	-25
-4	215	-212
-3	38	32
-2	199	20C
-1	46	-41
C	229	-202
1	11	14
2	187	192
3	15	-18
4	134	-126
5	11	14
6	106	108
7	15	-8
8	79	-81
9	14	1C

H,K= 4, 2

L	FOB	FCA
-11	9	6
-1C	61	67
-9	5	-9
-8	95	-89
-7	16	12
-6	147	137
-5	17	-13
-4	177	-167
-3	40	31
-2	193	184
-1	35	-3C
C	255	-214
1	22	27
2	166	157
3	21	-24
4	124	-116
5	11	1C
6	94	95
7	5	-1C
8	56	-60

H,K= 6, 2

L	FOB	FCA
-11	7	8
-1C	63	66
-9	9	-12
-8	98	-94
-7	7	1C
-6	124	117
-5	18	-12
-4	126	-12C
-3	16	14
-2	183	15C
-1	13	-13
C	183	-15C
1	20	22
2	132	118
3	10	-15
4	105	-104
5	12	11
6	69	72

H,K= 8, 2

L	FOB	FCA
-11	8	8
-1C	65	64
-9	10	-11
-8	94	-91
-7	15	15
-6	100	103
-5	19	-17
-4	109	-112
-3	12	12
-2	135	118
-1	11	-13
C	117	-99
1	9	12
2	97	91
3	6	-8
4	73	-76

H,K=1C, 2

L	FOB	FCA
-10	55	53
-9	6	-7
-8	65	-71
-7	10	11
-6	79	85
-5	12	-13
-4	97	-97
-3	18	14
-2	92	89
-1	13	-13
0	80	-77
1	12	8
2	70	69

H,K=12, 2

L	FOB	FCA
-7	7	6
-6	53	62
-5	12	-7
-4	64	-68
-3	9	9

H,K= 1, 3

L	FOB	FCA
-9	70	-68
-8	8	13
-7	95	94
-6	12	-9
-5	130	-125
-4	39	31
-3	170	160
-2	35	-30
-1	158	-154
0	35	29
1	150	156
2	58	-55
3	142	-137
4	26	26
5	108	106
6	17	-14
7	81	-87
8	16	17
9	47	57

H,K= 3, 3

L	FOB	FCA
-10	18	-14
-9	65	-68
-8	10	13
-7	97	92
-6	26	-23
-5	141	-131
-4	26	24
-3	158	153
-2	11	-4
-1	159	-161
0	42	30
1	139	155
2	36	-32
3	125	-118
4	15	16
5	95	96
6	22	-22
7	66	-70

H,K= 5, 3

L	FOB	FCA
-10	17	-10
-9	64	-66
-8	12	18
-7	96	89
-6	34	-31
-5	116	-111
-4	22	22
-3	127	124
-2	31	-21
-1	129	-140
0	33	27
1	116	125
2	16	-11
3	101	-103
4	12	16
5	80	82
6	16	-17

H,K= 7, 3

L	FOB	FCA
-10	13	-7
-9	67	-66
-8	15	15
-7	88	86
-6	12	-20
-5	95	-96
-4	22	22
-3	97	1C5
-2	28	-32
-1	97	-104
0	21	20
1	85	92
2	0	-13
3	81	-82
4	16	16

H,K= 9, 3

L	FOB	FCA
-9	55	-58
-8	9	10
-7	72	73
-6	8	-9
-5	78	-84
-4	16	17
-3	75	89
-2	17	-20
-1	69	-80
0	17	14
1	64	72
2	8	-16

H,K=11, 3

L	FOB	FCA
-7	49	55
-6	7	-10
-5	55	-65
-4	10	11
-3	55	66
-2	12	-9

H,K= 0, 4

L	FOB	FCA
0	148	137
1	39	-36
2	122	-116
3	37	35
4	101	97
5	16	-19
6	79	-82
7	11	17
8	48	55

H,K= 2, 4

L	FOB	FCA
-9	17	16
-8	64	64
-7	17	-15
-6	80	-82
-5	13	21
-4	99	93
-3	23	-25
-2	122	-119
-1	23	23
0	143	121
1	34	-37
2	110	-105
3	29	28
4	100	98
5	17	-22
6	70	-71
7	18	19

H,K= 4, 4

L	FOB	FCA
-9	13	15
-8	66	67
-7	24	-21
-6	78	-80
-5	27	28
-4	100	98
-3	22	-21
-2	121	-108
-1	21	24
0	114	96
1	19	-23
2	103	-94
3	17	18
4	84	81
5	19	-21
6	51	-56

H,K= 6, 4

L	FOB	FCA
-9	13	12
-8	58	60
-7	17	-21
-6	76	-77
-5	23	25
-4	91	94
-3	26	-27
-2	103	-91
-1	20	28
0	96	85
1	14	-18
2	87	-79
3	16	18
4	57	60

H,K= 8, 4

L	FOB	FCA
-8	48	51
-7	10	-13
-6	65	-66
-5	19	16
-4	75	76
-3	18	-22
-2	80	-75
-1	13	21
0	77	73
1	0	-18

H,K=10, 4

L	FOB	FCA
-5	12	12
-4	53	55
-3	16	-13

H,K= 1, 5

L	FOB	FCA
-7	44	-51
-6	24	22
-5	63	65
-4	19	-22
-3	76	-74
-2	23	27
-1	87	89
0	34	-29
1	86	-86
2	19	21
3	75	76
4	24	-22
5	64	-65
6	17	20

H,K= 3, 5

L	FCB	FCA
-7	52	-55
-6	13	19
-5	59	63
-4	22	-24
-3	70	-74
-2	28	31
-1	66	78
0	23	-25
1	63	-72
2	22	21
3	71	70
4	16	-22

H,K= 5, 5

L	FCB	FCA
-7	50	-53
-6	12	16
-5	60	64
-4	25	-23
-3	66	-73
-2	28	25
-1	55	67
0	26	-22
1	54	-65
2	16	23
3	50	56

H,K= 7, 5

L	FOB	FCA
-6	11	16
-5	53	58
-4	16	-19
-3	54	-62
-2	20	17
-1	49	61
0	15	-19

H,K= 0, 6

L	FCB	FCA
0	49	-55
1	18	21
2	52	55
3	16	-18

H,K= 2, 6

L	FCB	FCA
-3	18	22
-2	50	53
-1	20	-25
0	56	-54
1	12	19
2	56	53

H,K= 4, 6

L	FCB	FCA
-3	20	22
-2	49	50
-1	16	-22

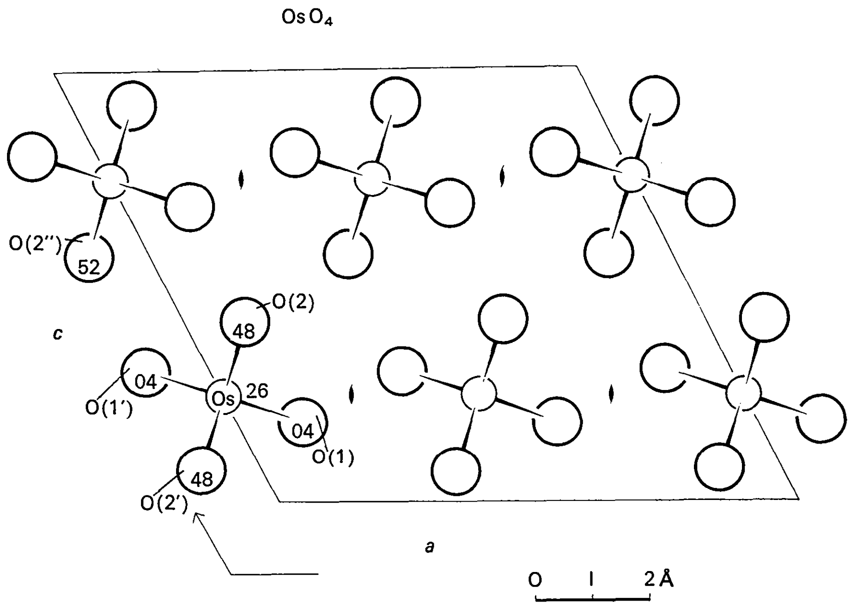

Fig. 2. Crystal structure of OsO_4. The *y* coordinates (multiplide by 100) are indicated for some atoms.

No coordinate changed as much as 0·001. The final parameters are listed in Tables 1 and 2, and the observed and calculated structure factors in Table 3.

Discussion

Bond lengths and angles are listed in Table 4 with standard deviations. The deviations from tetrahedral symmetry of the molecule are not experimentally significant. This result is in accord with the interpretation of Raman and infrared spectra by Woodward & Roberts (1956) and Dodd (1959). The average Os–O bond distance is $1{\cdot}74 \pm 0{\cdot}02$ Å, uncorrected for thermal motion. The r.m.s. interatomic distance is larger because of thermal motion by an amount which is estimated as 0·02 Å (with the assumption that oxygen rides on osmium), but the magnitude of this correction is doubtful because of the low precision of the thermal parameters. An early electron-diffraction study (Brockway, 1936) gave 1·66 Å for the Os–O distance, but this result is likely to be in error because of failure of the Born approximation (Glauber & Schomaker, 1953). A check on our result is given by the consistency of the isoelectronic sequence WO_4^{2-}, ReO_4^-, OsO_4, with bond distances W–O = 1·79 Å (Zalkin & Templeton, 1964; Kay, Frazer & Almodovar, 1964) and Re–O = 1·77 Å (Morrow, 1960).

The crystal structure (Fig. 2) can be described approximately as cubic closest packing of oxygen atoms, with osmium in tetrahedral holes. The pseudo-cubic pseudo-cell corresponding to the close packed oxygen structure has axes which are related to the monoclinic axes by the matrix $\frac{1}{2}\ 0\ \frac{1}{4}/\ 0\ 1\ 0\ /\ 0\ 0\ \frac{1}{2}$. From a different point of view, the structure can be described less accurately as cubic closest packing of OsO_4 molecules,

Table 4. *Interatomic distances and angles in* OsO_4, *with standard devations*

Atoms	Distance	Atoms	Angle
Os–O(1)	$1{\cdot}76 \pm 0{\cdot}03$ Å	O(1)–Os–O(1)	$110{\cdot}3 \pm 1{\cdot}9°$
Os–O(2)	$1{\cdot}71 \pm 0{\cdot}03$	O(1)–Os–O(2)	$110{\cdot}5 \pm 1{\cdot}3$
O(1)–O(1)	$2{\cdot}89 \pm 0{\cdot}06$	O(1)–Os–O(2′)	$107{\cdot}6 \pm 1{\cdot}3$
O(1)–O(2)	$2{\cdot}85 \pm 0{\cdot}04$	O(2)–Os–O(2′)	$110{\cdot}4 \pm 1{\cdot}9$
O(1)–O(2′)	$2{\cdot}80 \pm 0{\cdot}04$		
O(2)–O(2′)	$2{\cdot}81 \pm 0{\cdot}05$		

an arrangement which is common in crystals of spherical or nearly spherical molecules. The axes of the pseudo-cell describing this packing are derived from the monoclinic axes by the matrix $\frac{1}{2}\ 0\ -\frac{1}{2}\ /\ \frac{1}{2}\ 1\ \frac{1}{2}\ /\ \frac{1}{2}\ -1\ \frac{1}{2}$. In this packing each osmium atom has 12 osmium neighbors at distances ranging from 4·52 to 5·20 Å. The intermolecular O–O distances exceed 2·98 Å and are consistent with weak intermolecular forces indicated by the high vapor pressure and low melting point.

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