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Berkeley, California

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We have investigated the structure of solid osmium tetroxide by x-ray diffraction. Crystals, grown by sublimation, were sealed in Pyrex capillaries for the x-ray exposures because of their high vapor pressures. Rotation, oscillation, and Weissenberg photographs were taken with Cr Kα and Cu Kα radiation (λ = 2.2909 and 1.5418 A).

The structure is monoclinic, with $\underline{a}$ = 8.66 A, $\underline{b}$ = 4.52, $\underline{c}$ = 4.75, β = 117.9°, U = 164.3 A^3. With Z = 2, D_x = 5.14; D_m = 4.95 (Krauss and Schrader, 1928). The extinctions show the lattice to be C centered. The fact that all spots allowed by the C lattice are nearly equally intense, except for systematic variations due to absorption and angle factors, confirms that there are only two heavy atoms in the unit cell and shows that the oxygen atoms cannot be located by the present diffraction data.

The diffraction data permit space groups C2, Cm, and C2/m. Only with C2 is it possible to find a reasonable arrangement of the oxygen atoms. The OsO_4 molecule must be approximately tetrahedral. If it is taken as perfectly tetrahedral with the Os-O bond distance 1.66 A (Brockway, 1936), then the structure which gives the best intermolecular distances is:

Space group C2 - C_2^3

(000; 1/2 1/2 0) +

2 Os in 2(a) : (0$\underline{y}$0) with $\underline{y}$ = 0

4 O_I in 4(c) : ($\underline{x}$ $\underline{y}$ $\underline{z}$; $\bar{\underline{x}}$ $\underline{y}$ $\bar{\underline{z}}$)

with $\underline{x}$ = 0.13, $\underline{y}$ = 0.21, $\underline{z}$ = -0.07

4 O_{II} in 4(c) with $\underline{x}$ = 0.11, $\underline{y}$ = -0.21,

$\underline{z}$ = 0.31

In this structure, each oxygen atom has three oxygen neighbors in the same molecule, at 2.71 A, and six (for O_I) or seven (for O_{II}) neighbors in adjacent molecules at distances ranging from 2.90 to 3.25 A. The molecule is situated on a two-fold axis, so that deviations from tetrahedral symmetry are possible. For example, a twist of the O_I pair with respect to the O_{II} pair by 9° results in more nearly equal intermolecular distances (minimum distance 3.00 A) but with a simultaneous decrease in some of the intramolecular O-O distances to 2.59 A. Any change in the Os-O distance, of course, results in an inverse change in the minimum intermolecular O-O distances.

Except for the above structure, or small distortions of it, no structure could be found which gives reasonable interatomic distances. Therefore the x-ray data imply that the OsO_4 molecule is tetrahedral or nearly tetrahedral, even though oxygen positions cannot be derived from the observed intensities.

The crystals show twinning corresponding to reflection in the (001) plane. The shortest intermolecular O-O distances are between molecules whose centers are in this plane, and the structure can

be visualized as a layer structure. The twinning then involves only the method of stacking layers and does not disturb the shortest intermolecular contacts.

Some of the crystals were provided by Dr. C. R. Hurley. This research was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

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