

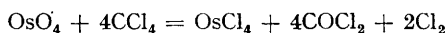
On the Polymorphism of Osmium Tetrachloride

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DEPENDING on the method of preparation, osmium tetrachloride may be obtained in two different crystalline modifications. These have been characterized by elemental analysis, X-ray powder diffractometry, and magnetic measurements.

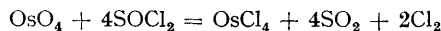
In particular, black osmium tetrachloride, previously synthesized from its elements,¹⁻³ has now been obtained by the action of carbon tetrachloride (saturated with chlorine gas) upon osmium tetroxide at 470° in a sealed glass tube. The following net reaction occurred:



The X-ray powder pattern of the black osmium tetrachloride, consisting of 26 lines, is tentatively indexed assuming an orthorhombic unit cell with the following dimensions: $a = 12.08$, $b = 11.96$, $c = 11.68$ Å. The main source of uncertainty arises from the fact that no measurements on single crystals could be performed. This chloride is paramagnetic and is characterized by an anomalously low temperature-independent⁴ susceptibility of $\chi_{\text{mole}} = +1080 \times 10^{-6}$ c.g.s. units. This low value is due to a strong spin-orbit coupling. However, no e.s.r. signal in the X-band region could be detected, either at 300 or at 77° K.

The second form of osmium tetrachloride was obtained at 80° C by heating under reflux a

solution of osmium tetroxide in thionyl chloride:



This dark brown chloride gives rise to a simple X-ray powder pattern (11 lines) from which the cubic lattice constant $a = 9.95$ Å could be deduced, although a trigonal unit cell could not be excluded. The compound is paramagnetic, but in contrast to the orthorhombic form the paramagnetism is slightly dependent upon temperature, with $\chi_{\text{mole}} = +880 \times 10^{-6}$ c.g.s. units (at 300° K). From these results it can be concluded that the orthorhombic form is the high-temperature form, whereas the cubic modification is the low-temperature one. Moreover, the slight difference between the unit-cell dimensions of the two modifications suggests that the orthorhombic modification may result from a distortion of the Jahn-Teller type acting upon the cubic form. The bond between the chlorine and the metal in the two modifications of osmium tetrachloride may be at least as strongly covalent as it is in K_2OsCl_6 (53%)⁵ and in some other noble-metal halides⁶ which already have been investigated by pure quadrupole spectroscopy.

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