Short Communications

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The unit cells and space groups of $SeCl_4$ and $TeCl_4$.

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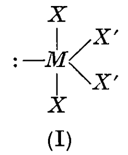
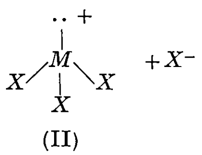
The structures of the Group VI tetrahalides in the solid state are assumed to be either trigonal bipyramidal molecules (I) or ionic structures containing pyramidal trihalide cations (II).



(I)



(II)

In these formulas M = S, Se, or Te, and X = halogen. In the gas phase the molecules are believed to have the structure shown in (I), with X–M–X' bond angles of approximately 90° and X'–M–X' angles of approximately 120°. This has been supported by electron diffraction studies of SF_4 (Kimura & Bauer, 1963; Ewing & Sutton, 1963), SeF_4 (Bowen, 1953) and $TeCl_4$ (Stevenson & Schomaker, 1940); microwave studies of SF_4 (Tolles & Gwinn, 1962); and the vibrational spectra of SF_4 (Dodd, Woodward & Roberts, 1956). The liquid states of SF_4 and SeF_4 have also been assigned this configuration on the basis of nuclear magnetic resonance spectra (Muetterties & Phillips, 1959; Cotton, George & Waugh, 1958). On the other hand, the solid compounds $SeCl_4$ and $TeCl_4$ are generally assumed to be of the ionic form shown in (II). This concept is based largely on the similarities of the Raman spectra of $SeCl_4$ and $TeCl_4$ to that of $AsCl_3$ and to those of the $SeCl_3^+$ cation obtained by dissolving $SeCl_4$ in $AlCl_3$ melt (Gerding & Houtgraaf, 1954). Contrary to this ionic concept, however, there are several physical properties of the tetrahalides, especially $TeCl_4$, that do not seem to be compatible with an ionic form. Most noteworthy is the solubility of $TeCl_4$ in non-polar organic solvents. In fact, recent work in this laboratory suggests that $TeCl_4$ dissolves in a molecular form in both benzene and the polar solvent nitrobenzene. In view of such apparent inconsistencies regarding the nature of the solid tetrahalides, we have begun an X-ray investigation of the Group VIA tetrahalides. In this note we would like to report the unit cells and space groups of $SeCl_4$ and $TeCl_4$.

Selenium tetrachloride was prepared by the direct reaction of chloride with gray powdered selenium. Yellow needle-like crystals elongated in the c direction were obtained by sublimation in a chlorine atmosphere, and the needles were transferred to, and sealed in, a 0·3 mm O.D. thin walled capillary tube under a chlorine atmosphere. Weissenberg photographs made with Cu $K\alpha$ radiation indicate an orthorhombic unit cell with

$$a = 23{\cdot}0, \quad b = 16{\cdot}5, \quad \text{and } c = 23{\cdot}5 \text{ Å}.$$

There are 64 molecules per unit cell, giving a calculated density of 2·63 g.cm^{-3} compared with an experimental density of 2·7 g.cm^{-3}. Systematic absences of hkl reflections for $(h+l)$ odd, of $0kl$ reflections for k odd and l odd, and of $hk0$ reflections for h odd and k odd indicate space group $Bbmb$ or $Bb-b$.

Tellurium tetrachloride was also prepared by the direct reaction of chlorine with tellurium metal. White needle-like crystals were obtained from carbon tetrachloride solution. These crystals were also sealed in capillary tubing to prevent hydrolytic decomposition. The needles were elongated in the c direction and twinned on (100). The unit cell parameters are

$$a = 15{\cdot}0, \quad b = 10{\cdot}0, \quad c = 15{\cdot}3 \text{ Å}; \quad \beta = 117°$$

Assuming 16 molecules per unit cell, the calculated density is 3·12 g.cm^{-3}, as compared with reported densities of 3·26 g.cm^{-3} (Beck, 1928) and 3·01 g.cm^{-3} (Honigschmid & Baudrexler, 1935). The absence of hkl reflections for $(h+k)$ odd, and of $h0l$ reflections for h odd and l odd indicate space group $C2/c$ or Cc.

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