Acta Cryst. (1965). **18**, 296

A note on the unit cells, space groups and structures of $SeCl_4$, $TeCl_4$ and $TeBr_4$.

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(*Received* 6 *August* 1964)

Cordes, Kruh, Gordon & Kemp (1964) have recently reported the unit cells and space groups of $SeCl_4$ and $TeCl_4$. Twelve years ago, crystals of these two compounds were prepared by Dr W. L. Groeneveld, at the Inorganic Chemistry Laboratory of the University of Leyden, Netherlands and studied by C. B. S. and Mrs E. Mellink-Maatman. Each crystal examined was twinned, and appeared to belong to the orthorhombic system. For $SeCl_4$, the corresponding unit-cell dimensions were

$$a' = 29{\cdot}34 \pm 0{\cdot}06,\ b' = 9{\cdot}73 \pm 0{\cdot}03,\ c' = 14{\cdot}93 \pm 0{\cdot}05\ \text{Å}$$

with space group *Bmam*, or lower.

$$D_m = 2{\cdot}6\ \text{g.cm}^{-3},\ D_x = 2{\cdot}73\ \text{g.cm}^{-3}$$

for 32 formula weights per cell.

Close examination of the intensity relationships revealed the true symmetry to be monoclinic, with cell dimensions as follows:

$SeCl_4$:
$a = 16{\cdot}46 \pm 0{\cdot}05,\ b = 9{\cdot}73 \pm 0{\cdot}03,\ c = 14{\cdot}93 \pm 0{\cdot}05$ Å;
$\beta = 117 \pm 0{\cdot}5°$.

$TeCl_4$:
$a = 16{\cdot}91 \pm 0{\cdot}05,\ b = 10{\cdot}36 \pm 0{\cdot}03,\ c = 15{\cdot}25 \pm 0{\cdot}05$ Å;
$\beta = 117 \pm 0{\cdot}5°$.

Space group $C2/c$ or Cc, $Z = 16$.

At about the same time, crystals of $TeBr_4$ were prepared by J. Kalnajs, at the Laboratory for Insulation Research, M.I.T. and examined by S. C. A., W. R. Blackmore and L. R. Lavine. These crystals were also twinned and apparently orthorhombic, with

$$a' = 31{\cdot}76 \pm 0{\cdot}05,\ b' = 10{\cdot}89 \pm 0{\cdot}02,\ c' = 15{\cdot}88 \pm 0{\cdot}02\ \text{Å}.$$

Subsequently, after a long search by the present authors, an untwinned crystal was found and shown to have lattice constants

$$a = 17{\cdot}75 \pm 0{\cdot}03,\ b = 10{\cdot}89 \pm 0{\cdot}02,\ c = 15{\cdot}88 \pm 0{\cdot}02\ \text{Å};\quad \beta = 116°\ 34' \pm 10',$$

with space group $C2/c$ or Cc.
$D_m = 4{\cdot}325\ \text{g.cm}^{-3}$, $D_x = 4{\cdot}326\ \text{g.cm}^{-3}$, assuming $Z = 16$.

The diffraction patterns of $SeCl_4$, $TeCl_4$ and $TeBr_4$ all contain a strong superlattice. These intense reflections correspond to a body-centered subcell of orthorhombic symmetry with cell edges $a'/8$, $b'/2$ and $c'/4$. Each subcell contains half a formula weight. The superlattice reflections are satisfied by placing the halogen atoms at the corners and body-center of the subcell, resulting in a slightly distorted cubic closest packing. Patterson projections indicated that the tellurium atoms are in the octahedral interstices of this halogen array, only one quarter of the interstices being occupied. In the real unit cell, the atoms must be slightly displaced from these ideal positions. These displacements could produce several arrangements. The Se and Te atoms could have four nearest neighbors, forming a distorted trigonal bipyramid (formula I of Cordes *et al.*, 1964); or they could have three nearest neighbors, forming a pyramidal $RHal_3^+$ ion (formula II of Cordes *et al.*). These are not the only configurations possible, but are considered those most likely.

A partial three-dimensional set of intensities was obtained from Weissenberg photographs, using Mo $K\alpha$ radiation, and the untwinned $TeBr_4$ crystal. The absorption was large, and no corrections were made. The resulting structure factors were of poor quality, and the traditional R index could not be reduced below 30%. An unambiguous distinction among formulae I and II above and other possible arrangements could not be made. It may be noted here that the crystal structure tentatively reported for TeI_4 (Blackmore, Abrahams & Kalnajs, 1956) contains an arrangement corresponding to formula I.

We wish to point out that our old results are in general agreement with those of Cordes *et al.* (1964) for $TeCl_4$, if it is assumed that their "a" value of 15·0 Å is really $a \sin \beta$. We did not, however, observe the large unit cell they report for $SeCl_4$, containing 64 formula weights. Although their orthorhombic b axis is the same length as our monoclinic a axis, it is not clear whether there are two different modifications of $SeCl_4$, or whether the unit cells only appear different owing to the operation of some, as yet undetermined, twin-law.

Note added in proof:—We have recently seen a communication by Khodadad, Laruelle & Flahaut (1964) reporting the lattice constants of $TeCl_4$ and $TeBr_4$. There constants, which are given to the nearest 0·1 Å, are consistent with ours.

References

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