and the mixed occupancy occurs in the two positions of intermediate coordination number (14).

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A Crystallographic Study of the Tellurium–Iodine System*

BY W. R. BLACKMORE†, S. C. ABRAHAMS‡ AND J. KALNAJS

Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A. and Chemistry Department, The University, Glasgow W. 2, Scotland

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Crystallographic data are given for the two stoichiometric compounds formed within the tellurium–iodine system. Tellurium tetraiodide crystallizes in the orthorhombic system with $a = 13·54 \pm 0·02$, $b = 16·73 \pm 0·02$ and $c = 14·48 \pm 0·02$ Å, space group *Pnma* or $Pn2_1a$. The other composition corresponds to Te_nI_n, and also crystallizes in the orthorhombic system, with $a = 8·23 \pm 0·03$, $b = 30·00 \pm 0·05$ and $c = 9·97 \pm 0·03$ Å, space group *Cmma* or *Cm2a*. The structure of a tetragonal crystal which may have been tellurium tetraiodide is described.

Introduction

The lattice constants of the terminal members of the tellurium–iodine system are well known. Tellurium is hexagonal with

$$a = 4·45564 \pm 0·00012, \quad c = 5·92685 \pm 0·00002 \text{ Å at } 18^\circ \text{ C}.$$

(Straumanis, 1940) and iodine is orthorhombic with

$$a = 4·784 \pm 0·001, \; b = 7·265 \pm 0·001 \text{ and } c = 9·792 \pm 0·002 \text{ Å}$$

(Heavens & Cheesman, 1950). Within this system, until the present investigation, the only well established stoichiometric compound had been tellurium tetraiodide. The structure of tellurium tetraiodide is of interest in a current study of 2-, 3- and 4-bonded compounds of the subgroup VI*b* elements. It was also thought desirable to re-examine the tellurium–iodine system by X-ray methods, even although the phase diagram had previously been investigated by thermal analysis (Jaeger & Menke, 1912; Damiens, 1923).

Experimental

Crystalline tellurium tetraiodide was prepared either by heating tellurium tetrabromide with ethyl iodide (Montignie, 1947) or by reacting the elements in a modification of Damiens' (1923) method. In this modification, the elements are mixed in the requisite proportions, and sealed off in a small-volume Pyrex tube in an atmosphere of nitrogen. Since tellurium melts at 452° C., the tube is heated to about 500° C. for 2–3 hr., to ensure completion of the reaction. The resulting black crystals of tellurium tetraiodide take the form of plates and bipyramids.

Intermediate compositions were prepared in the same manner, from the melt. The preparation corresponding to Te_nI_n was further annealed for 15 hr. at about 120° C. and cooled slowly to promote crystal growth.

The single-crystal X-ray diffraction measurements were recorded using Weissenberg and precession cameras with Mo $K\alpha$ ($\lambda = 0·7107$ Å) radiation. With microcrystalline samples, the Norelco wide-range diffractometer and also the 114·59 mm. diameter powder camera were used with Cu $K\alpha$ ($\lambda = 1·5418$ Å) radiation.

Crystal data for orthorhombic tellurium tetraiodide

All preparations except that referred to in the foot-

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† Present address: Central Research Laboratory, Canadian Industries (1954) Limited, McMasterville, Quebec, Canada.

‡ Present address: Chemistry Department, The University, Glasgow W. 2, Scotland.

note* gave orthorhombic crystals, with lattice constants

$$a = 13{\cdot}54 \pm 0{\cdot}02,\ b = 16{\cdot}73 \pm 0{\cdot}02 \text{ and } c = 14{\cdot}48 \pm 0{\cdot}02 \text{ Å}.$$

Absent reflexions: $(0kl)$ with $k+l = 2n+1$ and $(hk0)$ with $h = 2n+1$. Space group: $Pnma\text{–}D_{2h}^{16}$ or $Pn2_1a\text{–}C_{2v}^{9}$. $D_m = 5{\cdot}056$ g.cm.$^{-3}$ (Damiens, 1923), $D_X = 5{\cdot}145$ g.cm.$^{-3}$. There are 16 formula weights per unit cell. Volume of the cell is 3280·1 Å^3, volume per molecule is 205·0 Å^3. Analysis of the crystals, obtained from the melt, gave 81·65% iodine; calculated for TeI_4 gives 79·91% iodine.

The crystal structure of this modification has not yet been investigated. In order to determine whether the orthorhombic crystal might possess a transition point, the diffraction pattern was studied down to liquid-nitrogen temperatures, using the techniques of Abrahams & Kalnajs (1954). The pattern remains essentially unchanged between 25° C. and −190° C.

Intermediate compositions in the tellurium–iodine system

In Damiens' (1923) thermal study of the tellurium–iodine system, there was no unambiguous evidence for the formation of any new compound. In the present study, seven compositions in the range between Te and TeI_4 were prepared, and their powder patterns were recorded. Corresponding to the composition with equal parts of tellurium and iodine, a new set of reflexions was observed. This composition has the molecular formula Te_nI_n. The spacings characteristic of this composition become discernible at a concentration of about 20% by weight of iodine. At about 50% concentration the intensities diffracted by the Te_nI_n crystals reach a maximum, although a slight indication of the 101 tellurium reflexion is still present. At about a concentration of 70% iodine, the characteristic pattern of Te_nI_n diminishes to zero. There is apparently no solid solution of Te_nI_n in either Te or TeI_4.

It has been pointed out by McCullough (1954) that if the new compound is regarded as Te_2I_2, the formula would compare closely with the analogous compounds S_2Cl_2 and Se_2Br_2.

Crystal data for Te_nI_n

Small soft deformed single crystals were cut out from the annealed ingot of composition Te_nI_n. These crystals are orthorhombic with

$$a = 8{\cdot}23 \pm 0{\cdot}03,\ b = 30{\cdot}00 \pm 0{\cdot}05 \text{ and } c = 9{\cdot}97 \pm 0{\cdot}03 \text{ Å}.$$

Absent reflexions: (hkl) with $h+k = 2n+1$, $(0kl)$ with $k = 2n+1$, $(h0l)$ with $h = 2n+1$ and $(hk0)$ with $h, k = 2n+1$. Space group: $Cmma\text{–}D_{2h}^{21}$ or $Cm2a\text{–}C_{2v}^{15}$. $D_m = 5{\cdot}31$ g.cm.$^{-3}$, $D_X = 5{\cdot}49$ g.cm.$^{-3}$. There are 16 Te_2I_2 formula weights per unit cell. Volume of the unit cell is 2461·6 Å^3.

It is a pleasure to thank Dr E. Grison, who prepared the photographs of tetragonal 'tellurium tetraiodide' in 1950, and Professors A. von Hippel and J. M. Robertson for their interest in this study.

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[*] A few crystals in one preparation were found having the form of regular bipyramids. These crystals were tetragonal, with

$$a = 16{\cdot}12 \pm 0{\cdot}04 \text{ and } c = 11{\cdot}20 \pm 0{\cdot}02 \text{ Å},$$

the c axis being the pyramidal axis. Absent reflexions: (hkl) with $h+k+l = 2n+1$, $(hk0)$ with $h = 2n+1$, and $k = 2n+1$, and (hhl) with $2h+l = 4n$. Space group was hence uniquely $I4_1/amd\text{–}D_{4h}^{19}$. Neither the observed density nor a confirmatory chemical analysis could be obtained, owing to lack of material, in spite of repeated preparations. $D_X = 5{\cdot}79$ g.cm.$^{-3}$, assuming 16 TeI_4 formula weights per unit cell. Volume of the cell is 2910·3 Å^3 and of each molecule is 182·0 Å^3.

Assuming these crystals were indeed tellurium tetraiodide, a molecular model based upon an octahedral bond distribution for the tellurium atom was obtained, with the tellurium atom in the $16(h)$ position at $(0, \frac{1}{8}, \frac{3}{8})$ and the iodine atoms in the $16(h)$ and $32(i)$ positions, at $(0, \frac{1}{8}, \frac{1}{8})$, $(0, \frac{1}{8}, \frac{5}{8})$ and $(\frac{1}{8}, \frac{1}{4}, \frac{3}{8})$. This model was refined by the method of least squares, and gave a moderately good fit with the observed $(hk0)$ and $(h0l)$ structure factors: $R(hk0) = 0{\cdot}18$ and $R(h0l) = 0{\cdot}27$. Because of the considerable overlap in projection, three-dimensional data were needed to effect further refinement. It did not prove possible to obtain these extra data, since the original crystal was lost and no other crystal of tetragonal symmetry could be isolated.

It is thought, however, that the general agreement among the measured and calculated structure factors, together with the reasonable molecular model (cf. the bond distribution in di-p-tolyl selenium dichloride (McCullough & Marsh, 1950)) were evidence in favor of these crystals being tellurium tetraiodide.