Tellurium-125 Mössbauer Spectra of Some Tellurium Subhalides

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The ^{125}Te Mössbauer spectra at 4.2 K for the crystalline tellurium subhalides Te_3Cl_2, Te_2X (X = Br or I), $Te_2Br_{0.75}I_{0.25}$, β-TeI, and α-TeI show the presence of at least two different tellurium sites in each subhalide in accordance with their known crystal structures. The chemical isomer shifts δ (relative to $Zn^{125m}Te$ at 4.2 K) in four different types of co-ordination have been found to be 0.6 mm s^{-1} for trigonal bipyramidal tellurium atoms $[Te(Te)_2(Cl)_2E]$, 0.8—1.0 mm s^{-1} for square-planar (pseudo-octahedral) tellurium atoms $[Te(Te)_2(X)_2E_2]$ (X = Br or I), 0.3—0.8 mm s^{-1} for trigonal pyramidal (pseudo-tetrahedral) tellurium atoms $[Te(Te)_2(X)E]$ (X = Te or I), and 0.8 mm s^{-1} for two-co-ordinate (pseudo-tetrahedral) tellurium atoms $[Te(Te)_2E_2]$. The symbols in square brackets indicate the nearest-neighbour environment of the relevant tellurium atom, the symbol E being used to represent an essentially non-bonding pair of electrons. The corresponding quadrupole splittings for the four environments were 11.0, 12.1—13.7, 3.4—6.1, and 8.1 mm s^{-1} respectively. The bonding scheme for square-planar tellurium atoms in the tellurium subhalides is considered to involve two three-centre four-electron bonds and is thus similar to that in the isostructural and isoelectronic species $[ICl_4]^-$ and $XeCl_4$. The Mössbauer spectra at 4.2 K for the glassy phases $Te_2Br_{0.75}I_{0.25}$ and $TeBr_2$ were different from those of the corresponding crystalline compounds but again showed the existence of at least two different tellurium sites in each compound.

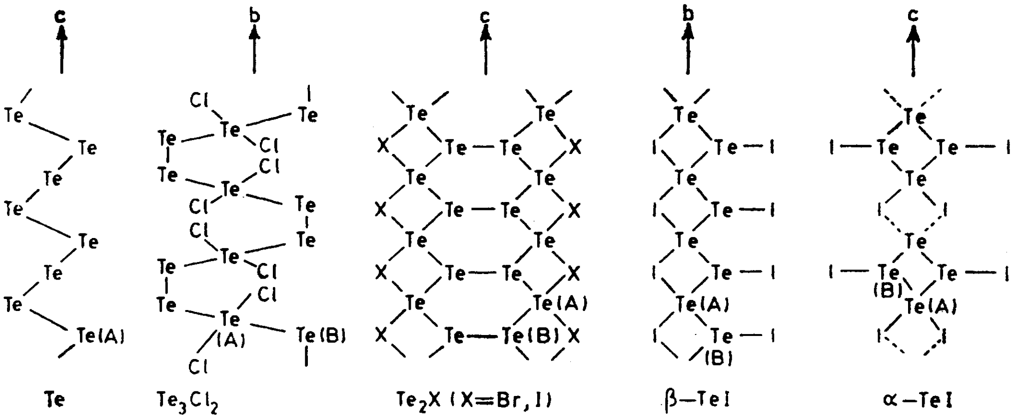

FIGURE 1 Schematic structures of tellurium and its subhalides

TELLURIUM-125 Mössbauer spectroscopy has previously been used to study a number of halogen-containing compounds of tellurium in which the formal oxidation state of tellurium is II, IV, or VI.[1-3] Recently the existence of several tellurium subhalides has been established [4] and the crystal structures of Te_3Cl_2,[5,6] Te_2X (X = Br or I),[5,6] β-TeI,[6,7] and α-TeI [6,7] have been determined. These structures reveal at least two different tellurium sites in each subhalide. The abnormally low formal oxidation states of the subhalides pose interesting problems of chemical bonding and we decided to measure their Mössbauer spectra in order to obtain further insight into the bonding and stereochemistry obtaining in these compounds. Before presenting our results, however, it will be helpful to summarize the known structural features of the subhalides. These are shown schematically in Figure 1 together with that of elemental

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tellurium in which the three-fold screw axis lies parallel to the crystallographic *c*-axis.[8]

The local environment of each tellurium atom in elementary tellurium can be represented as $[Te(Te)_2E_2]$ where E represents a non-bonding pair of electrons. The building unit of Te_3Cl_2[5,6] is also an infinite Te-screw: two tellurium atoms are each co-ordinated by two other tellurium atoms in a similar way to that of elementary tellurium but each third tellurium atom also binds two chlorine atoms axially. The co-ordination of this tellurium atom is trigonal-bipyramidal if the non-bonding pair of electrons E is included in the co-ordination scheme, $[Te(Te)_2(Cl)_2E]$.

Crystals of the type Te_2X (X = Br or I) [5,6] and β-TeI [6,7] consist of zig-zag chains of tellurium atoms in a planar arrangement. Along the chain there is an alternation of trigonal-pyramidal (pseudo-tetrahedral) and square planar (pseudo-octahedral) tellurium atoms. In Te_2X, pairs of these tellurium zig-zag chains are cross linked at every second tellurium atom (trigonal-pyramidal) along the chain, resulting in a ribbon of six-membered tellurium rings with the boat conformation. The two tellurium environments can be summarized as $[Te(Te)_3E]$ and $[Te(Te)_2(X)_2E_2]$. Likewise, β-TeI features the same local stereochemistry but the directly bonded groups comprise two tellurium atoms and one terminal iodine atom for the trigonal-pyramidal tellurium $[Te(Te)_2(I_t)E]$, and two tellurium atoms and two bridging iodine atoms for the square-planar tellurium $[Te(Te)_2(I_b)_2E_2]$.

By contrast, the structural unit of α-TeI [6,7] is not an infinite polymeric chain or ribbon but a tetrameric molecule Te_4I_4 in which there are two trigonal-pyramidal tellurium atoms $[Te(Te)_2(I_t)E]$ and two slightly different square-planar tellurium atoms. In one of these the tellurium is strongly co-ordinated within the molecular unit as $[Te(Te)_2(I_t)_2E_2]$ whereas in the other, the two-co-ordinate tellurium atom of the Te_4I_4 molecule is weakly co-ordinated intermolecularly by the terminal iodine atoms on the square-planar tellurium atom of the next Te_4I_4 molecule along the *c* axis, as shown by the dotted lines in Figure 1, *i.e.* $[Te(Te)_2E_2 \cdots (I_t)_2]$. The average intermolecular bond distance Te ··· I is 3.38 Å which is 8—10% longer than the average Te(square-planar)–I_b bond length of 3.13 Å in Te_2I [5,6] and β-TeI,[6,7] and the average Te(square-planar)–I_t bond length of 3.08 Å in α-TeI.

RESULTS AND DISCUSSION

Mössbauer Spectra of the Tellurium Subhalides.—Typical spectra for the polycrystalline, single-crystal, and glassy compounds and for elementary tellurium are shown in Figures 2—5. The best computer fitting of the data (except for Te_3Cl_2) was obtained under the constraint that the four absorption lines due to two quadrupole doublets had equal width at half height. For Te_3Cl_2 the best fit was obtained by constraining both the inner two peaks and the outer two peaks separately to have the same width and the same intensity within each pair. The resulting full experimental line widths at half maximum resonance, Γ, are listed in the Table together with the χ^2 values and number of degrees of freedom. The narrower line width for Te_2I is due to the use of an improved narrow-line source of $^{125}Sb/Cu$ for this experiment.

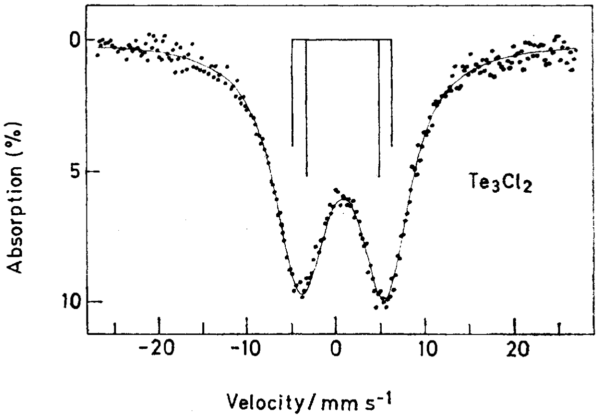

FIGURE 2 ^{125}Te Mössbauer spectrum of Te_3Cl_2 at 4.2 K relative to $Zn^{125m}Te$ at 4.2 K

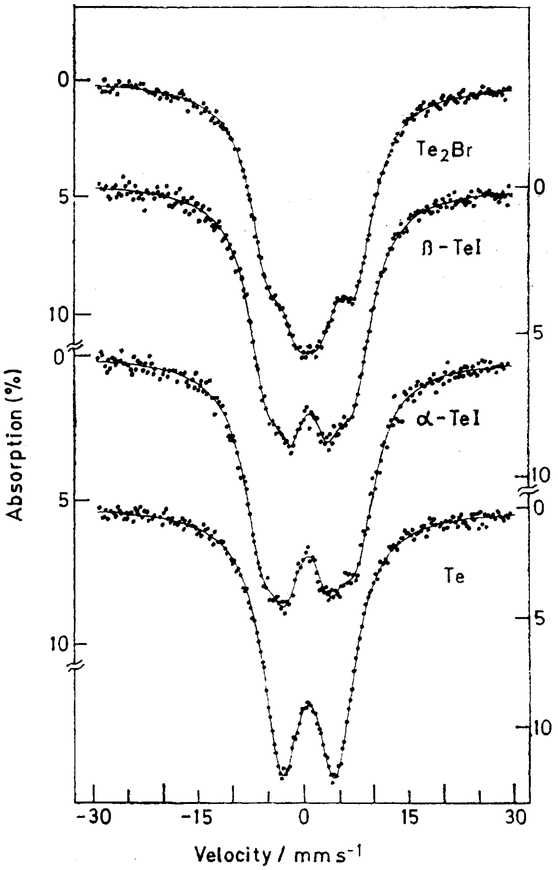

FIGURE 3 ^{125}Te Mössbauer spectra of polycrystalline Te_2Br, β-TeI, α-TeI, and Te at 4.2 K relative to $Zn^{125m}Te$ at 4.2 K

The ^{125}Te Mössbauer parameters at 4.2 K for the two sites Te(A) and Te(B) are also given in the Table, though it should be noted that the designations (A) and (B) do not necessarily correspond to the same tellurium site symmetries for each compound (see Figure 1). The parameters for the six polycrystalline compounds are followed by those for a single crystal of α-TeI, for the two glassy compounds, and for the single site in elementary tellurium. The chemical isomer shifts, δ, are relative to the $Zn^{125}Te$ source at 4.2 K and the quadrupole splittings, ΔE_Q, are also listed. The absorption intensity is the experimentally observed percentage decrease in count rate from the base line without correction for background. The absorption area ratios of the individual components of the outer doublets A_1/A_4 and inner doublets A_2/A_3 are also given as well as the overall absorption area ratios of the two sites Te(A) and Te(B), *i.e.* the area ratio of the outer doublet to the inner doublet.

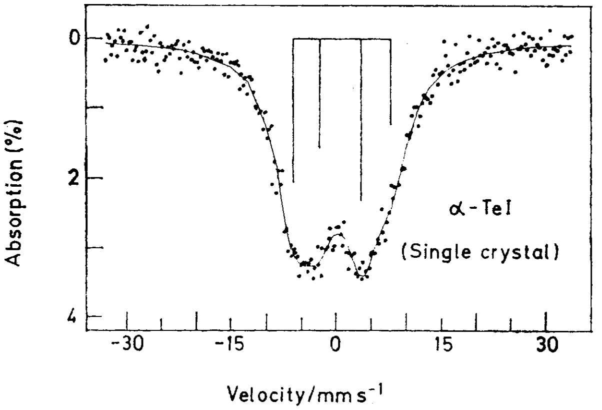

FIGURE 4 ^{125}Te Mössbauer spectrum of α-TeI single-crystal at 4.2 K relative to $Zn^{125m}Te$ at 4.2 K

Mössbauer parameters for tellurium subhalides at 4.2 K

	Te(A)				Te(B)						
Compound	δ * mm s⁻¹	ΔE_Q mm s⁻¹	Absorption intensity (%)	Area ratio A_1/A_4	δ * mm s⁻¹	ΔE_Q mm s⁻¹	Absorption intensity (%)	Area ratio A_2/A_3	Γ mm s⁻¹	Area ratio Te(A)/Te(B)	χ^2/degrees of freedom
Te_3Cl_2	0.63(10)	11.0(8)	4(1), 4(1)	1.0(4)	0.78(12)	8.1(3)	5(1), 5(1)	1.0(3)	6.3(5) 6.5(3)	0.78(19)	221/231
Te_2I	0.81(8)	12.23(16)	1.6(1), 2.5(1)	0.64(5)	0.32(16)	3.42(15)	2.1(1), 1.9(1)	1.08(11)	5.53(16)	1.00(6)	233/231
$Te_2Br_{0.75}I_{0.25}$	1.01(4)	12.13(9)	5.0(1), 5.1(1)	0.98(4)	0.76(9)	3.80(8)	5.3(1), 5.4(2)	0.98(5)	6.41(9)	0.94(3)	227/231
Te_2Br	0.89(3)	12.57(7)	5.5(1), 6.4(1)	0.87(3)	0.59(8)	3.35(7)	6.0(2), 5.8(2)	1.04(5)	6.28(8)	1.00(3)	277/231
β-TeI	0.81(5)	12.67(11)	4.7(2), 5.0(1)	0.95(5)	0.67(8)	5.11(9)	5.1(2), 5.1(1)	1.00(5)	6.13(10)	0.95(3)	236/231
α-TeI	0.78(6)	13.72(13)	4.5(2), 4.8(2)	0.94(6)	0.49(7)	6.08(11)	5.1(2), 5.0(2)	1.03(6)	6.34(13)	0.92(4)	270/231
α-TeI (sing. cryst.)	1.0(2)	13.9(3)	2.1(2), 1.3(1)	1.7(2)	0.7(2)	6.0(3)	1.6(2), 2.3(1)	0.7(1)	6.6(3)	0.85(7)	196/231
$Te_2Br_{0.75}I_{0.25}$ (glassy)	0.69(2)	10.73(16)	7.1(4), 7.1(4)	1.00(9)	0.6(1)	5.1(4)	2.9(4), 2.9(4)	1.0(3)	6.8(4)	2.5(3)	273/231
Te_2Br (glassy)	0.63(5)	10.64(13)	7.4(4), 7.7(3)	0.97(6)	0.5(2)	4.8(3)	2.7(3), 2.5(3)	1.1(2)	6.78(8)	2.9(3)	240/231
Te	0.63(2)	7.60(3)	10.6(1), 10.7(1)	1.00(2)					6.50(8)		202/243

* Relative to $Zn^{125m}Te$ source at 4.2 K.

Assignment of the Mössbauer Parameters.—The Table shows that the area ratio Te(A)/Te(B) is close to unity for polycrystalline Te_2X (X = Br or I), $Te_2Br_{0.75}I_{0.25}$, β-TeI, and α-TeI, as expected from the equal populations of tellurium atoms in the square-planar and trigonal-pyramidal sites. In Te_3Cl_2, however, the inner doublet due to Te(B) has a substantially larger absorption area than the outer doublet: this indicates that Te(B) refers to two-co-ordinate tellurium whereas the outer doublet Te(A) arises from the trigonal-bipyramidal tellurium atoms, since the site population of the two-co-ordinate tellurium site is twice that of the trigonal-bipyramidal site. It will be noted that the Mössbauer parameters (δ and ΔE_Q) of the two-fold co-ordinated Te(B) atoms of Te_3Cl_2 are similar to those of tellurium metal, as expected from the similar co-ordination around tellurium in both materials. The trigonal-bipyramidal Te(A) site has the larger quadrupole splitting. The area ratios of the individual components of each quadrupole doublet (A_1/A_4 and A_2/A_3) are essentially unity for the polycrystalline samples other than Te_2I. The observed asymmetry for the outer doublet of Te_2I is probably due to preferential orientation, since the needle-like crystals were not powdered (see Experimental section). The Mössbauer spectrum of the oriented single-crystal sample of α-TeI exhibits an even larger asymmetry in both quadrupole doublets because of the angular dependence of the individual components. This enables Te(A) to be assigned to the square-planar site and Te(B) to the trigonal-pyramidal site by the following argument.

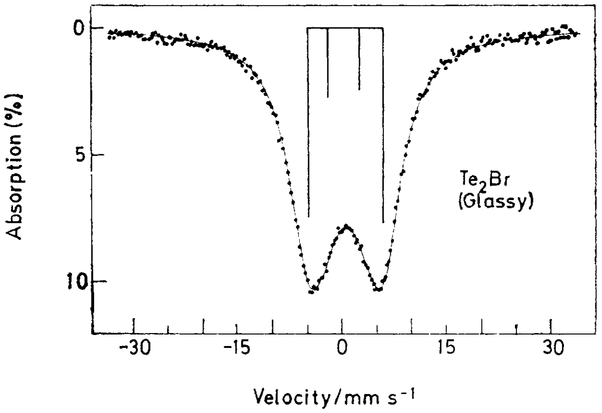

FIGURE 5 ^{125}Te Mössbauer spectrum of glassy Te_2Br at 4.2 K relative to $Zn^{125m}Te$ at 4.2 K

For the $\frac{1}{2} \longrightarrow \frac{3}{2}$ Mössbauer transition in ^{125}Te, the angular dependence of the relative intensities of the quadrupole doublet components is given by

$$\frac{I(\pm\frac{1}{2} \longrightarrow \pm\frac{3}{2})}{I(\pm\frac{1}{2} \longrightarrow \pm\frac{1}{2})} = \frac{3(1 + \cos^2\theta)}{5 - 3\cos^2\theta}$$

where θ is the angle between the z axis of the electric field gradient (e.f.g.) and the incident γ-rays.[9] The e.f.g. at the nucleus is produced by the aspherical electronic charge distribution. For the square-planar tellurium atoms, bonding can be considered to involve two three-centre four-electron bonds in the xy plane:[10] this leaves two non-bonding pairs of electrons in the $5s$ and $5p_z$ atomic orbitals of the central tellurium atom. This imbalance in the $5p$ orbital population produces an e.f.g. with its principal (z) axis along the $5p_z$ orbital and perpendicular to the square-plane. The sign of V_{zz} (= eq) is therefore negative. As the nuclear quadrupole moment of the excited state of ^{125}Te, $Q_e(+\frac{3}{2})$, is negative,[11,12] this means that the quadrupole coupling constant e^2qQ/h will be positive. The Mössbauer resonance arising from the $\pm\frac{1}{2} \longrightarrow \pm\frac{3}{2}$ transition thus appears at more positive velocity than that arising from the $\pm\frac{1}{2} \longrightarrow \pm\frac{1}{2}$ transition. It is next necessary to determine the angle θ between the axis normal to the square-plane and incident γ-ray. From the known crystal structure of α-TeI and the experimental geometry this angle was found to be 90°. Thus, in the triclinic crystal of α-TeI as shown in Figure 6, the local Te z axes [which pass through the square-planar Te(1) and Te(4) and are normal to these square-planes] are necessarily parallel to the ac plane which is also the plane of cleavage.[13] In the single-crystal Mössbauer experiment on α-TeI, the plate-like crystals were placed in the γ-ray beam in such a way that the cleavage surfaces were normal to the incident γ-ray. The required angle θ is, thus, 90° and the equation gives 1 : 1.67 as the ratio of the relative intensities of the quadrupole doublet components. It follows that the Mössbauer resonance due to the square-planar Te atoms should have a low-velocity absorption peak which is 1.67 times as strong as the high-velocity component.

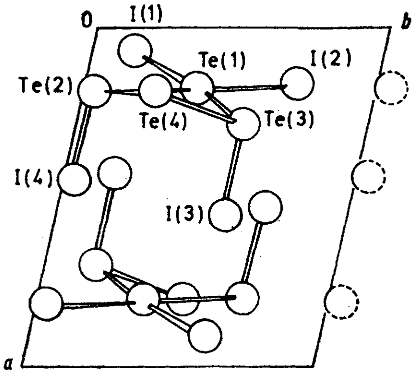

FIGURE 6 Arrangement of the Te$_4$I$_4$ molecules in α-TeI; the structure is projected down the c^*-axis onto the ab plane[6]

The actual Mössbauer spectrum of single-crystal α-TeI (Figure 3) shows that the outer doublet [referred to as Te(A) in the Table] corresponds closely to this expectation, the observed absorption area ratio being 1.7 ± 0.2 as predicted. Accordingly, the outer doublet, with a quadrupole splitting of 13.7 mm s^{-1}, is assigned to the square-planar Te(A) atom and the inner doublet with a quadrupole splitting of 6.1 mm s^{-1} to the trigonal-pyramidal Te(B) atom.

The z axis of the e.f.g. for Te(A) was taken to be normal to the square-plane defined by the surrounding two tellurium and two iodine atoms. These four atoms were considered to be bonded to Te(A) *via* two three-centre four-electron bonds. Consistent with this model, it is worthy of note that the square-planar Te(A) in α-TeI has almost the same value of V_{zz} (= eq) as those for the isostructural and isoelectronic halides of iodine and xenon, where the bonds are generally thought to involve only $5p$ electrons of iodine and xenon.[14,15] The details of the calculation are as follows. The quadrupole coupling constants $e^2q^{127}Q_g/h$ for ^{127}I in the ICl$_4$ units in I$_2$Cl$_6$, I$_2$Cl$_4$Br$_2$, and KICl$_4$·H$_2$O are 3 060, 3 040, and 3 094 MHz respectively and the value for the ICl$_2$Br$_2$ unit in I$_2$Cl$_4$Br$_2$ is 2 916 MHz,[14] leading to a mean value of 3 028 MHz. Likewise, $e^2q^{129}Q_e/h$ for ^{129}Xe in XeCl$_4$ is 1 640 MHz.[15] The quadrupole splitting for ^{125}Te in the TeTe$_2$I$_2$ unit in α-TeI is 13.7 mm s^{-1}; this corresponds to a value for $e^2q^{125}Q_e/h$ of 783 MHz assuming (as implied by the structure) a negligible value for the asymmetry parameter η, so that $\Delta E_Q = \frac{1}{2}e^2qQ_e/h$. (For ^{125}Te 1 mm s^{-1} = 28.63 MHz.) The appropriate nuclear quadrupole moments, Q, for ^{127}I, ^{129}Xe, and ^{125}Te are -0.78,[16] -0.41,[17] and -0.19 barns,[11,12] respectively. Remembering that 1 barn = 10^{-28} m^2, $e = 1.602 \times 10^{-19}$ C and $h = 6.626 \times 10^{-34}$ J s, this leads to essentially the same value of V_{zz} (= cq) for square-planar ^{127}I (-1.61×10^{23} V m^{-2}), ^{129}Xe (-1.65×10^{23} V m^{-2}), and ^{125}Te (-1.70×10^{23} V m^{-2}). It is also noteworthy that, in the ICl$_4$ units where $5p_x$ and $5p_y$ electrons are removed from iodine to form the I–Cl bonds, a valence-shell configuration of $5s^25p_z^25p_x^{0\cdot65}5p_y^{0\cdot65}$ has been derived for the central iodine atom.[14]

Comparisons can also be drawn between the large quadrupole splittings of 13.7 mm s^{-1} for the square-planar Te(A) in α-TeI and similar large quadrupole splittings of 15.2—17.4 mm s^{-1} which have recently been reported for the isostructural and isoelectronic Te$^{\text{II}}$ complexes of thiourea and its derivatives where Te$^{\text{II}}$ is bound to either four sulphur atoms or two sulphur atoms and two halogen atoms in a square-plane.[18] Accordingly, for crystalline Te$_2$X (X = Br or I), Te$_2$Br$_{0.75}$I$_{0.25}$, β-TeI, and α-TeI it seems reasonable to assign the Te(A) resonance, which has the more positive chemical-isomer

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shift (0.8—1.0 mm s^{-1}) and larger quadrupole splitting (12.1—13.7 mm s^{-1}) in the Table, to the tellurium in square-planar co-ordination. It follows that the Te(B) atoms for these compounds, which have chemical isomer shifts in the range 0.3—0.8 mm s^{-1} and quadrupole splittings in the range 3.4—6.1 mm s^{-1}, should be assigned to the tellurium in trigonal-pyramidal co-ordination. It can also be seen that trigonal-pyramidal tellurium atoms co-ordinated by three other Te atoms in Te_2X (X = Br or I) and $Te_2Br_{0.75}I_{0.25}$ have smaller quadrupole splittings than the corresponding tellurium atoms co-ordinated by two Te atoms and one I atom in β-TeI and α-TeI.

Chemical Isomer Shifts of the Tellurium Subhalides.—The sign of $\Delta R/R$ is positive for ^{125}Te so that the more positive the chemical isomer shift the larger the *s*-electron density at the nucleus.[1] Removal of one 5*s* electron is expected to decrease the ^{125}Te chemical isomer shift by *ca.* 2.4 mm s^{-1}, since the ^{129}I chemical isomer shift decreases by 8.2 mm s^{-1} for the removal of one 5*s* electron [14] and the ratio of these chemical isomer shifts, both relative to the ZnTe source, $(^{125}\delta/^{129}\delta)$ZnTe, is known to be +0.29.[19] The removal of 5*p* electrons increases the *s* electron density at the nucleus because of the decrease in shielding. It is reported that the ^{125}Te chemical isomer shift increases by *ca.* 0.4 mm s^{-1} for each 5*p* electron removed and that, when there is no 5*s*-participation in the bonding, the chemical isomer shift relative to Zn^{125m}Te is given by

$$(^{125}\delta)\mathrm{ZnTe} = +0.44\, h_p - 0.16 \text{ mm s}^{-1}$$

where h_p is defined as the number of 5*p* electron holes in the closed Te^{2-} shell.

Since the 5*s* orbital is considered not to participate appreciably in the bonding in square-planar Te atoms as discussed above, we can estimate the 5*p* orbital electron population by using the above equation. The observed average chemical isomer shift for the square-planar tellurium atoms is 0.86 mm s^{-1} which gives an h_p value of 2.32, implying a valence shell configuration of $5s^2 5p_z^2 5p_x^{0.8} 5p_y^{0.8}$ for tellurium. This configuration is quite consistent with the observed large quadrupole splittings of 12—14 mm s^{-1}.

The chemical isomer shift of 0.6 mm s^{-1} for the trigonal-bipyramidal tellurium atom in Te_3Cl_2 and of 0.3—0.8 mm s^{-1} for the trigonal-pyramidal tellurium atom in Te_2X (X = Br or I), $Te_2Br_{0.75}I_{0.25}$, β-TeI, and α-TeI are smaller than those of 0.8—1.0 mm s^{-1} for square-planar tellurium atoms. This may be due to some 5*s*-participation in the bonding in trigonal-bipyramidal and trigonal-pyramidal tellurium.

Glassy Tellurium Subhalides.—The Mössbauer spectra of glassy $Te_2Br_{0.75}I_{0.25}$ and Te_2Br were very similar to each other but different from those of the corresponding crystalline forms. The spectrum of Te_2Br is shown in Figure 5. Detailed analysis of these spectra shows the presence of at least two different sites in the glassy form, one having δ = 0.6—0.7 mm s^{-1}, ΔE_Q = 10.7 mm s^{-1}, and the other having δ = 0.5—0.6 mm s^{-1}, ΔE_Q = 5.0 mm s^{-1}. These Mössbauer parameters differ from those of the corresponding crystalline compounds (see Table). Furthermore, the absorption area ratio of the two sites is not unity as observed for the crystalline form but 2.5(3) : 1 and 2.9(3) : 1 for glassy $Te_2Br_{0.75}I_{0.25}$ and Te_2Br respectively. These facts suggest a different structure in the glassy and crystalline forms. It has previously been proposed from the radial distribution function of the glassy $Te_2Br_{0.75}I_{0.25}$ as determined by *X*-ray diffraction that the tellurium zig-zag chain structure is maintained over a distance of *ca.* 16 Å.[20] The large quadrupole splitting observed suggests that the square-planar co-ordination remains around the Te(A) atoms which form the zig-zag chains.

EXPERIMENTAL

Materials.—Samples of crystalline Te_3Cl_2, Te_2I, $Te_2Br_{0.75}I_{0.25}$, Te_2Br, β-TeI, and α-TeI and glassy $Te_2Br_{0.75}I_{0.25}$ and Te_2Br were kindly supplied by R. Kniep, Düsseldorf.

Mössbauer Measurements.—^{125}Te Mössbauer spectra were obtained with a spectrometer comprising an MVT3 transducer, an MD3 drive amplifier, and an MFG3 wave-form generator, all from Elscint Ltd., and an NS 630 multichannel analyser from Northern Scientific Inc. Both source and absorber were kept at 4.2 K in an MHC-3 liquid helium cryostat from Elscint Ltd. Transmission geometry was used, and the 6.9 keV escape peak generated by the 35.5 keV γ-rays of the source was detected by means of an NaI(Tl) crystal 0.13 mm thick. Counts were accumulated in half of the 1 024 channels available.

Sources were obtained from the Radiochemical Centre, Amersham. A nominal 10 mCi Zn^{125m}Te source ($t_{\frac{1}{2}}$ = 58 d) was used in all the measurements except for Te_2I, for which a 1 mCi ^{125}Sb/Cu source ($t_{\frac{1}{2}}$ = 2.7 y) was used. Comparison of the spectra of tellurium metal obtained from both sources indicated that the experimental line width (Γ) of 5.93(8) mm s^{-1} observed for ^{125}Sb/Cu was smaller than the corresponding value of 6.50(8) mm s^{-1} for Zn^{125m}Te. The chemical isomer shifts (δ) of tellurium metal relative to the Zn^{125m}Te and ^{125}Sb/Cu sources were 0.63(2) and 0.47(3) mm s^{-1}. Accordingly, the value of δ for Te_2I quoted in the Table with respect to Zn^{125m}Te was calculated by adding 0.16 mm s^{-1} to the value of δ obtained with ^{125}Sb/Cu. To enhance the flux of the Mössbauer γ-rays at the detector relative to the far more intense tellurium *X*-rays, a copper foil 0.25 mm thick was placed in front of the Zn^{125m}Te source, and the copper *X*-rays generated in this foil were attenuated by an 0.5-mm thick aluminium absorber placed in front of the detector. For the ^{125}Sb/Cu source, only the aluminium absorber was used.

The samples (except for Te_2I and the single crystals of α-TeI) were finely powdered and the absorbers contained 35-mg Te per cm^2 (*i.e.* 2.5 mg ^{125}Te per cm^2). To avoid decomposition of Te_2I into elementary tellurium and iodine, the needle-like crystals were mounted in a sample holder without previous grinding. For the single-crystal measurements on α-TeI, three plate-like crystals were mounted together in the sample holder with their large

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surfaces of cleavage (5 × 9 mm^2, 3 × 5 mm^2, and 2 × 5 mm^2) at right angles to the γ-ray beam. The absorber thickness was 73 mg of Te per cm^2 (*i.e.* 5.1 mg ^{125}Te per cm^2).

The total number of counts per channel was in the range (1.1—5.6) × 10^5 after folding the mirror-image spectra. The data were fitted by Lorentzian lines using established computer programmes.[21] The velocity scale of the spectrometer was calibrated by means of a Mössbauer spectrum of ^{57}Fe metal. Zero velocity was also checked by measuring the Mössbauer spectrum of $BaSnO_3$ against a source of $Ba^{119m}SnO_3$.

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