Tellurium-125 Mössbauer Spectra of Some Mixed Oxides of Tellurium(IV) and Some Mixed-valence Oxides of Tellurium(IV, VI)

By **Masuo Takeda** and **Norman N. Greenwood,*** Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT

^{125}Te Mössbauer spectra of 10 tellurium(IV)–oxygen compounds of accurately known crystal structure and six other such compounds of unknown structure have been recorded. Data have also been obtained for the mixed-valence oxides Te_2O_5 and Te_4O_9. The results establish the oxidation states where these were uncertain and show that the mixed-valence oxides are $Te^{IV}Te^{VI}O_5$ and $Te^{IV}_3Te^{VI}O_9$ respectively. Quadrupole splittings generated by the stereochemically active lone pair of electrons on Te^{IV} have been correlated with the extent of distortion of the oxygen co-ordination polyhedra and decrease in the sequence type (A) ≥ (B) ≥ (C). The ^{57}Fe Mössbauer spectrum of $Fe_2Te_3O_9$ shows that the compound is magnetically ordered at 4.2 K, but the ^{125}Te spectrum indicates that there is no detectable transferred hyperfine field at the tellurium nucleus. The ^{119}Sn Mössbauer spectrum of $SnTe_3O_8$ confirms the presence of Sn^{IV} in this compound.

COMPOUNDS of tellurium(IV), with an electron configuration $[Kr]4d^{10}5s^2$, occasionally have highly symmetrical co-ordination polyhedra around the Te^{IV} atom but more often they have non-symmetrical co-ordination polyhedra due to the presence of a stereochemically active lone pair of electrons.[1] The ^{125}Te Mössbauer transition is well suited to study such effects and it is already known that $TeCl_4$ gives a quadrupole-split spectrum [2,3] implying a stereochemically active lone pair, whereas the complexes $[TeCl_6]^{2-}$ and $[TeBr_6]^{2-}$ are precisely octahedral and show no quadrupole splitting; [4] these latter complexes have an unusually high chemical isomer shift due to the stereochemically inert $5s^2$ lone pair.[4] Several Mössbauer studies have also been made on various tellurium(IV)–oxygen compounds such as α-TeO_2 (paratellurite),[3-7] $Te_2O_4{\cdot}HNO_3$,[3,4] Na_2TeO_3,[2,4,6,7] $MTeO_3$ (M = Sr, Ba, or Cu),[4] H_2TeO_3,[3] $[NH_4]_2TeO_3$,[3] and $Na_2TeO_3{\cdot}5OH_2$,[2] though it has not previously been possible to give a general interpretation of the observed quadrupole splittings.

The detailed crystal structures of the following tellurium(IV)–oxygen compounds have appeared in the literature: MTe_3O_8 (M = Ti, Zr, Hf, or Sn),[8] UTe_3O_9,[9] $NaVTeO_5$,[10] α-$TeVO_4$,[11] β-$TeVO_4$,[12] $V_2Te_2O_9$,[13] and $UTeO_5$.[14] Accordingly we have examined the Mössbauer spectra of these well characterized new compounds and some other tellurium(IV)–oxygen compounds in order to discover possible correlations between the ^{125}Te Mössbauer parameters and the local symmetry about the Te^{IV} sites. In addition the crystal structure of the mixed-valence oxide Te_2O_5 has recently been reported [15] and this provided the incentive to record the first Mössbauer spectra of the two mixed-valence $Te^{IV,VI}$ oxides Te_2O_5 and Te_4O_9.

RESULTS AND DISCUSSION

The Mössbauer parameters at 80 K for the Te^{IV} compounds studied are listed in Table 1. The first 10 compounds have precisely known structures and these are

---

[1] J. Galy, N.B.S. Special Publication 364, 'Solid State Chemistry,' *Proc. 5th Materials Res. Symp.*, July 1972, p. 29.

[2] P. Jung and W. Triftshäuser, *Phys. Rev.*, 1968, **175**, 512.

[3] M. L. Unland, *J. Chem. Phys.*, 1968, **49**, 4514.

[4] T. C. Gibb, R. Greatrex, N. N. Greenwood, and A. C. Sarma, *J. Chem. Soc. (A)*, 1970, 212.

[5] N. Shikazono, *J. Phys. Soc. Japan*, 1963, **18**, 925.

[6] C. E. Violet and R. Booth, *Phys. Rev.*, 1966, **144**, 225.

[7] N. E. Erickson and A. G. Maddock, *J. Chem. Soc. (A)*, 1970, 1665.

[8] G. Meunier and J. Galy, *Acta Cryst.*, 1971, **B27**, 602.

[9] J. Galy and G. Meunier, *Acta Cryst.*, 1971, **B27**, 608.

[10] J. Darriet, G. Guillaume, K.-A. Wilhelmi, and J. Galy, *Acta Chem. Scand.*, 1972, **26**, 59.

[11] G. Meunier, J. Darriet, and J. Galy, *J. Solid State Chem.*, 1972, **5**, 314.

[12] G. Meunier, J. Darriet, and J. Galy, *J. Solid State Chem.*, 1973, **6**, 67.

[13] J. Darriet and J. Galy, *Cryst. Struct. Comm.*, 1973, **2**, 237.

[14] G. Meunier and J. Galy, *Acta Cryst.*, 1973, **B29**, 1251.

[15] O. Lindqvist and J. Moret, *Acta Cryst.*, 1973, **B29**, 643.

followed by six compounds of less certain crystal structure.* Within each group the sequence followed is one of gradually decreasing quadrupole splitting, ΔE_Q. Table 1 also contains data for the mixed-valence oxides Te^{IV}-$Te^{VI}O_5$ and $Te^{IV}{}_3Te^{VI}O_9$ and for $H_2Te^{VI}O_4$. The chemical isomer shifts, δ, are recorded relative to the source ^{125}I–Cu and the Table also lists the full experimental linewidth at half maximum height (Γ). The percentage absorption intensity is the experimentally observed decrease in count rate from the base line without correction for background. Typical spectra are shown in Figure 1. The data were computer fitted under the constraint that both components of the quadrupole doublet had equal width at half height. χ^2 Values and numbers of degrees of freedom are listed in the final column of Table 1. The Te^{IV} compounds (I)—(XVI) had chemical isomer shifts in the range 0.5—0.9 mm s^{-1}, *i.e.* appreciably more positive than the value of -1.22 mm s^{-1} for $H_2Te^{VI}O_4$, (XIX). This is consistent with the expected higher 5*s*-electron density at the ^{125}Te nucleus.[4] It is also noteworthy that the results for $SnTe_3O_8$, (II), and $Fe_2Te_3O_9$, (XV), establish that all the tellurium in these compounds is in the oxidation state IV; this deduction was confirmed from their ^{119}Sn and ^{57}Fe Mössbauer spectra which were typical of Sn^{IV} and high-spin Fe^{III} respectively (see footnotes to Table 1 for numerical data).

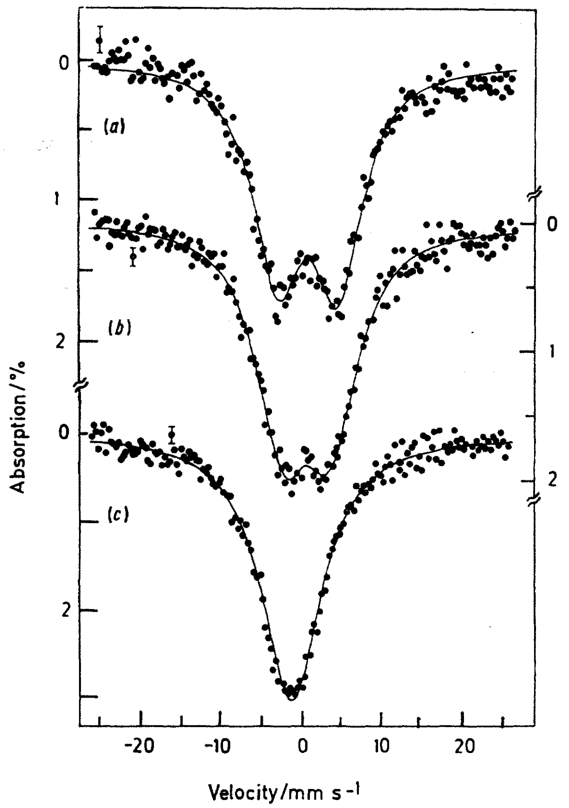

FIGURE 1 ^{125}Te Mössbauer spectra of (*a*) UTe_3O_9, (*b*) α-$TeVO_4$, and (*c*) H_2TeO_4 at 80 K relative to the ^{125}I–Cu source at 80 K

^{125}Te Mössbauer spectra of certain paramagnetic and mixed-valence compounds were also recorded at 4.2 K and the results are in Table 2. Typical spectra are in Figure 2. The chemical isomer shifts are *ca.* 0.1 mm s^{-1} less than those in Table 1 and the quadrupole splittings are on average *ca.* 0.3 mm s^{-1} less than those obtained at 80 K. The substantial decrease in linewidth (*ca.* 1 mm s^{-1}) of the spectra at 4.2 K is almost entirely due to the improved linewidth of the Zn–^{125m}Te source used for the experiments at liquid-helium temperature. The substantial increase in absorption intensity at 4.2 K is also notable, and this explains the change of scale on the axes of Figures 1 and 2.

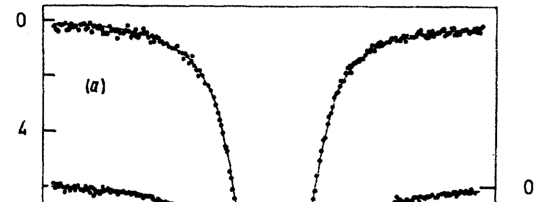

FIGURE 2 ^{125}Te Mössbauer spectra of (*a*) $Fe_2Te_3O_9$, (*b*) α-$TeVO_4$, (*c*) Te_2O_5, and (*d*) Te_4O_9 at 4.2 K relative to the Zn–^{125m}Te source at 4.2 K

The ^{57}Fe spectrum of $Fe_2Te_3O_9$, (XV), at 4.2 K showed magnetic-hyperfine interaction with a flux density of 49.7(1) T [*i.e.* 497(1) kG]. Despite this, the

---

* *Note added at proof:* The structure of $LiVTeO_5$, (XII), has now been determined (J. Darriet, *Bull. Soc. France Mineral. Crist.*, to be published) and the co-ordination around Te^{IV} is of type B, consistent with the quadrupole splitting recorded in Table 1. The compounds $Al_2Te_3O_9$, (XIV), and $Cr_2Te_3O_9$, (XVI), should now be formulated as $Al_2Te_4O_{11}$ and $Cr_2Te_4O_{11}$ (despite their synthesis from $M_2O_3 + 3\ TeO_2$) on the basis of single-crystal *X*-ray studies (J. Galy, personal communication). The co-ordination around Te^{IV} is of type C as predicted from the Mössbauer data in Table 1. The structure of Te_4O_9, (XVIII), has now been determined (O. Lundqvist, W. Mark, and J. Moret, *Acta Cryst.*, to be published). The Te^{IV} has a distorted trigonal-bipyramidal structure with four close Te–O distances of 1.883, 1.902, 2.020, and 2.144 Å; the co-ordination is thus of type B, consistent with the quadrupole splitting listed in Table 1.

linewidths of the ^{125}Te spectrum of this compound are virtually the same as for non-magnetic $Al_2Te_3O_9$, (XIV), implying that there is no significant transferred hyperfine field at the tellurium nucleus in (XV). Likewise, there was no detectable broadening in the ^{125}Te spectra of β-$TeVO_4$, (V), or $Cr_2Te_3O_9$, (XVI), which contain the $3d^1$ V^{IV} ion and the $3d^3$ Cr^{III} ion respectively. However, as can be seen from Figure 2, α-$TeVO_4$, (X), gave an unusual Mössbauer spectrum at 4.2 K; this is clearly not a simple quadrupole-split spectrum as would be expected on the basis of its known structure at room temperature and suggests the possibility of a previously unsuspected low-temperature phase transition. Accordingly, several models were tried for computer fitting. The best results were obtained by assuming two quadrupole-split doublets and this led to the data in Table 2. The relative intensities of the two pairs of peaks were 1 : 1.16 implying approximately equal numbers of tellurium atoms on the presumed two sites.

TABLE 1

Mössbauer parameters for tellurium–oxygen compounds at 80 K

Compound	δ [a]	ΔE_Q	Γ	Absorption	χ^2 (degrees of freedom)
		mm s^{-1}		(%)	
UTe_3O_9 (I)	+0.74(7)	7.48(10)	7.34	1.4, 1.5	190 (190)
$SnTe_3O_8$ (II) [b]	+0.69(9)	7.34(11)	8.20	1.3, 1.5	253 (190)
$ZrTe_3O_8$ (III)	+0.68(9)	7.13(12)	7.70	1.2, 1.2	215 (190)
$HfTe_3O_8$ (IV)	+0.89(10)	7.10(13)	7.57	1.2, 1.3	200 (190)
β-$TeVO_4$ (V)	+0.57(7)	7.00(9)	8.32	1.5, 1.6	203 (190)
$TiTe_3O_8$ (VI)	+0.73(6)	6.95(7)	7.53	1.7, 1.7	163 (190)
$V_2Te_2O_9$ (VII)	+0.66(9)	6.88(12)	7.16	1.1, 1.1	254 (190)
$NaVTeO_5$ (VIII)	+0.63(8)	6.70(10)	8.05	1.4, 1.2	246 (190)
$UTeO_5$ (IX)	+0.63(8)	6.55(10)	7.95	1.5, 1.5	211 (190)
α-$TeVO_4$ (X)	+0.73(7)	6.04(9)	7.89	1.5, 1.5	251 (190)
$Sc_{0\cdot5}Ta_{0\cdot5}Te_3O_8$ (XI)	+0.78(7)	7.32(9)	7.49	1.2, 1.3	195 (190)
$LiVTeO_5$ (XII)	+0.63(7)	7.06(10)	7.26	1.5, 1.6	239 (190)
$Nb_2Te_2O_9$ (XIII)	+0.85(10)	6.55(13)	7.86	1.3, 1.3	291 (190)
$Al_2Te_3O_9$ (XIV)	+0.71(13)	6.70(11)	8.21	1.0, 1.0	262 (190)
$Fe_2Te_3O_9$ (XV) [c]	+0.51(11)	6.69(13)	7.71	1.1, 1.2	217 (190)
$Cr_2Te_3O_9$ (XVI)	+0.31(13)	6.25(11)	7.49	0.9, 1.0	276 (190)
Te_2O_5 (XVII)	+0.79(20)	6.74(46)	6.65	3.1, 2.2	190 (182)
	−0.78(43)	0.0	7.96	4.2	
Te_4O_9 (XVIII)	+0.73(24)	6.85(46)	6.68	2.7, 3.1	191 (183)
	−1.05(79)	0.0	6.68	1.9	
H_2TeO_4 (XIX)	−1.22(4)	0.0	8.99	3.0	233 (197)

[a] Relative to the ^{125}I–Cu source; data for Te_2O_5 and Te_4O_9 were obtained with a Zn–^{125m}Te source and converted into the ^{125}I–Cu standard by substracting 0.12 mm s^{-1}. [b] In addition ^{119}Sn Mössbauer parameters (mm s^{-1}) at 80 K were δ (relative to $BaSnO_3$ at 80 K) −0.072(2), ΔE_Q 0.0, and Γ 1.34(1); at 294 K the values were δ (relative to $BaSnO_3$ at 294 K) −0.084(2), ΔE_Q 0.0, and Γ 1.15(1), typical of Sn^{IV}. [c] In addition ^{57}Fe Mössbauer parameters (mm s^{-1}) at 80 K were δ (relative to metallic Fe at room temperature) 0.486(3), ΔE_Q 0.548(5), and Γ 0.38(1), 0.34(1); at 294 K the values were δ (relative to metallic Fe at room temperature) 0.385(2), ΔE_Q 0.370(3), and Γ 0.30(1), 0.28(1), typical of high-spin Fe^{III}.

TABLE 2

Mössbauer parameters for tellurium–oxygen compounds at 4.2 K

Compound	δ [a]	ΔE_Q	Γ	Absorption	χ^2 (degrees of freedom)
		mm s^{-1}		(%)	
UTe_3O_9 (I)	+0.67(2)	7.08(2)	6.55, 6.61	10.0, 9.9	242 (242)
β-$TeVO_4$ (V)	+0.60(2)	6.59(1)	6.98, 6.99	11.8, 12.4	380 (247)
α-$TeVO_4$ (X)	+0.50(3)	3.10(11)	6.44, 6.44	5.5, 5.5	223 (233)
	+0.75(1)	8.37(11)	6.44, 6.44	6.4, 6.4	
$Al_2Te_3O_9$ (XIV) *	+0.37(3)	6.54(3)	6.67, 6.73	4.8, 4.8	227 (244)
$Fe_2Te_3O_9$ (XV) [b]	+0.47(2)	6.42(2)	6.96, 6.77	8.2, 8.1	242 (244)
$Cr_2Te_3O_9$ (XVI) *	+0.38(2)	6.31(2)	6.67, 6.88	11.0, 11.0	267 (244)
Te_2O_5 (XVII)	+0.45(2)	6.90(5)	6.42, 6.42	7.0, 7.0	273 (233)
	−0.90(2)	0.0	7.04	11.2	
Te_4O_9 (XVIII)	+0.56(7)	6.91(7)	6.68, 6.68	6.2, 9.4	259 (232)
	−1.24(14)	0.0	6.68	6.7	
H_2TeO_4 (XIX) [c]	−1.22(1)	0.0 [c]	7.75	20.6	372 (244)
TeO_3 (XX)	−1.18(1)	0.0	7.78	18.3	367 (244)

Relative to ^{125}I–Cu at 80 K, calculated by subtracting 0.12 mm s^{-1} from the experimentally observed shifts from a Zn–^{125m}Te source at 4.2 K. [b] In addition, ^{57}Fe Mössbauer parameters (mm s^{-1}) at 4.2 K were δ (relative to metallic Fe at room temperature) 0.512(5), quadrupole interaction $(e^2qQ/8)$ $(3\cos^2\theta - 1)$ −0.128(5), and magnetic flux density B 49.7(1)T (*i.e.* 497 kG). [c] The χ^2 value was improved to 242 (235) by using a two-peak fit; this gave ΔE_Q 1.79(7) mm s^{-1}.

The compounds H_2TeO_4, (XIX), and TeO_3, (XX), both showed rather large resonance linewidths. It is significant that (XIX) contains distorted $Te^{VI}O_6$ octahedra with Te^{VI}–O bond distances in the range 1.903—1.930 Å,[16] and it may well be that this asymmetry engenders the incipient unresolved quadrupole splitting of *ca.* 1.8 mm s^{-1} at 4.2 K.

---

[16] J. Moret, E. Philippot, M. Maurin, and O. Lindqvist, *Acta Cryst.*, 1974, **B30**, 1813.

Mössbauer spectra of Te_2O_5, (XVII), at 80 and 4.2 K showed the presence of both Te^{IV} and Te^{VI} atoms as distinct structural units. The ratio of the absorption area of the Te^{IV} doublet to that of the Te^{VI} singlet at 80 K was **1.1(5)** : 1 and at 4.2 K was **1.13(5)** : 1. This is consistent with the known *X*-ray crystal structure of the compound, in which there are equal numbers of Te^{IV} and Te^{VI} atoms,[15] and implies similar Mössbauer recoil-free fractions for the two entities. Similarly the spectra of Te_4O_9, (XVIII), at 80 and 4.2 K are interpreted as the superposition of a Te^{IV} quadrupole doublet and a Te^{VI} singlet. The ratio of the two areas was determined as $3.0 \pm 2.4 : 1$ at 80 K and $2.3 \pm 0.3 : 1$ at 4.2 K. The crystal structure of this compound is not yet known * but, bearing in mind experimental problems such as saturation effects and possible small variations in recoil-free fractions at various sites in the lattice, the Mössbauer results favour the formulation $Te^{IV}{}_3Te^{VI}O_9$.

As can be seen from Tables 1 and 2, substantial quadrupole splittings were observed for all the tellurium(IV)–oxygen compounds studied; this implies substantial deviations of the tellurium(IV)–oxygen co-ordination polyhedra from cubic symmetry. According to Galy[1] there are two types of oxygen co-ordination to Te^{IV} as illustrated in (A) and (C), and very recently Brown[17] has suggested that there is also an intermediate type of co-ordination as illustrated in (B). In type (A), *e.g.* $SnTe_3O_8$, (II),[8] the co-ordination polyhedron around Te^{IV} can be described as a trigonal bipyramid of oxygen atoms with one equatorial apex occupied by the non-bonding pair of electrons. The two equatorial bonds Te–O(1) and Te–O(2) are shorter than the two axial bonds Te–O(3) and Te–O(4) and there are two further oxygen atoms O(5) and O(6) which are repelled to longer distances by the presence of the non-bonding pair of electrons in the same plane. There are thus two short, two intermediate, and two long Te–O distances in the distorted octahedral environment around the tellurium atom. In type (C), *e.g.* α-$TeVO_4$, (X),[11] the tellurium atom is co-ordinated by three oxygen atoms O(1), O(2), and O(3) to form a trigonal pyramid with short Te–O bonds and there are three additional oxygen atoms O(4), O(5), and O(6) at longer distances to complete the octahedron. The non-bonding pair of electrons is presumably located on the diagonal between these three long Te–O bonds. In the intermediate configuration (B) there is a partial lengthening of one of the two intermediate Te–O distances in (A); this arrangement is found, for example, in β-$TeVO_4$ (V).[12]

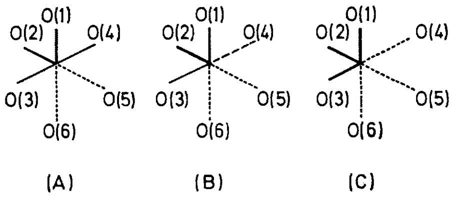

TABLE 3

Structural parameters of tellurium–oxygen compounds

Compound		Te–O Bond lengths (Å) O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O–Te–O Bond angles (°) O(1)–O(2)	O(1)–O(3)	O(2)–O(3)	O(3)–O(4)	Config.	Ref.
UTe_3O_9	(I)	1.78	2.02	2.15	2.16	2.55	2.82	95.8			156.6	(A)	9
$SnTe_3O_8$	(II)	1.87	1.87	2.12	2.12	2.93	2.93	102.9			156.8	(A)	8
$ZrTe_3O_8$	(III)	1.96	1.96	2.16	2.16	2.97	2.97	102.5			156.3	(A)	8
$HfTe_3O_8$	(IV)	1.89	1.89	2.16	2.16	2.99	2.99	104.9			157.6	(A)	8
β-$TeVO_4$	(V)	1.85	1.87	2.02	2.20	2.95	3.19	95			147	(B)	12
$TiTe_3O_8$	(VI)	1.85	1.85	2.12	2.12	2.93	2.93	102.2			159.2	(A)	8
$V_2Te_2O_9$	(VII)	1.84	1.86	1.92	2.68 [a]	2.96 [a]	3.34 [a]	100.4	90.3	94.9		(C)	13
Te_2O_5	(XVII)	1.89	1.91	2.07	2.08	3.16 [b]	2.71	91.0	86	86	165.9	(A)	15
$NaVTeO_5$	(VIII)	1.93	1.94	2.04	2.15	2.75 [b]	2.84 [b]	94 [b]	90 [b]	88 [b]	167 [b]	(B)	10
$UTeO_5$	(IX)	1.88	1.96	1.89	2.24	2.95	3.05	101.5	81	74 [b]	150.8	(B)	14
α-$TeVO_4$	(X)	1.81	1.95	1.99	2.58	2.78	2.80	92.0	98.5	94.0	164 [b]	(C)	11

[a] Calculated in the present work from data in ref. 13. [b] From ref. 17.

The known structural parameters for tellurium(IV)–oxygen compounds are summarized in Table **3** together with the assigned configuration. Although $NaVTeO_5$ was assigned to type (A) by Brown,[17] we prefer to place it in type (B) because of the appreciable difference in the distances Te–O(3) and Te–O(4). Since it has been found[18] that $Sc_{0\cdot5}Ta_{0\cdot5}Te_3O_8$, (XI), is isostructural with $TiTe_3O_8$, (VI), and since, moreover, the Sc^{III} and Ta^{V} atoms are distributed statistically on the Ti^{IV} sites, the oxygen environment around Te^{IV} is likely to be similar and (XI) is accordingly assigned to type (A). The compound $LiVTeO_5$, (XII), crystallizes in the orthorhombic system; its detailed structure is not known though it is not isostructural with $NaVTeO_5$, (VIII), which crystallizes in the monoclinic system.[19] The crystal structures of $M_2Te_3O_9$ [(XIV)—(XVI); M = Al, Fe, or Cr] are not yet known * though (XIV) and (XVI) are isomorphous.[20] The compound $Nb_2Te_2O_9$, (XIII), may well have the (C) type arrangement similar to that of $V_2Te_2O_9$, (VII).

In an attempt to see if there was any correlation between Mössbauer parameters and types of co-ordination polyhedra where these were known, the quadrupole

---

* See foonote on p. 2208.

[17] I. D. Brown, *J. Solid State Chem.*, 1974, **11**, 214.

[18] G. Meunier, J. Galy, and P. Hagenmuller, *Compt. rend.*, 1970, **C270**, 1987.

[19] J. Darriet, G. Guillaume, and J. Galy, *Compt. rend.*, 1970, **C269**, 23.

[20] B. Frit and P. Hagenmuller, *Bull. Soc. chim. France*, 1970, 2491.

splittings at 80 K were plotted as a function of chemical isomer shift using a code which indicated structure type. The result is shown in Figure 3. Compounds (I)—(III), (IV), (VI), (XI), and (XVII) in Table 1 have type (A) co-ordination and quadrupole splittings in the range 7.5—6.7 mm s^{-1}. The type (B) compounds (V), (VIII), and (IX) have values of ΔE_Q in the range 7.0—6.5 mm s^{-1}, whereas the type (C) compounds (VII), (X), and possibly (XIII) fall in the range 6.9—6.0 mm s^{-1}. There is some overlap in these ranges but they follow the sequence (A) $\geqslant$ (B) $\geqslant$ (C). A similar trend was observed at 4.2 K. It is perhaps unfortunate that two of the three compounds with unknown structure in Table 1 [*viz.* (XIV)—(XVI)] fall in the region of overlap at 6.7 mm s^{-1}, though it seems clear that $Cr_2Te_3O_9$, (XVI), is likely to have type (C) co-ordination (three short plus three long Te–O distances).*

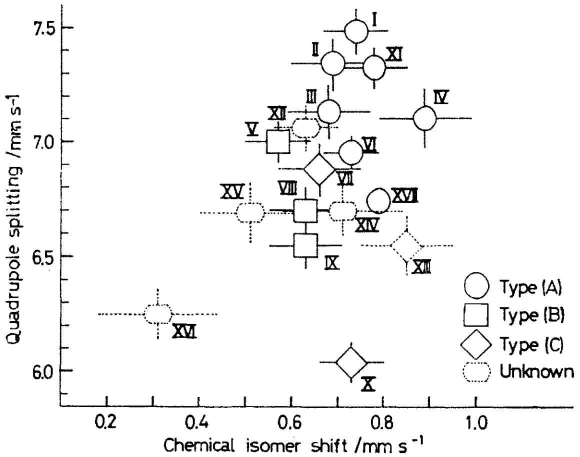

FIGURE 3 Plot of quadrupole splitting against chemical isomer shift at 80 K. Numbers refer to the compounds listed in Table 1, types refer to the stereochemistry, and the straight lines indicate standard deviations in the data

The present data can also be compared with previously published values for ΔE_Q of Te^{IV} compounds at liquid-nitrogen temperature. Thus, α-TeO_2 with type (A) co-ordination [17,21] has a quadrupole splitting of 6.7 mm s^{-1} (a mean of four values [3,4,6,7]). Likewise, $Te_2O_4 \cdot HNO_3$ [type (B) [22]] has ΔE_Q 6.65 mm s^{-1}.[4] The compound Na_2TeO_3 has ΔE_Q 6.2 mm s^{-1} (a mean of values from refs. 2, 4, 6, and 7) and the compounds $MTeO_3$ (M = Sr, Ba, and Ca) fall in the range 6.0—6.5 mm s^{-1},[4] consistent with their expected type (C) co-ordination. It is also significant that the chloro-compound $TeCl_4$, which in the solid state contains $TeCl_6$ octahedra distorted in a similar way to the (C)-type arrangement,[23] also has relatively small values for ΔE_Q at liquid-nitrogen temperature, published values being [2,3] 4.0 ± 1.6 and 5.4 ± 0.8 mm s^{-1}.

It is not possible at present to give a rigorous interpretation of the decreasing magnitude of the electric-field gradient (e.f.g.) at the Te^{IV} nucleus as the oxygen co-ordination changes from type (A) through (B) to (C). It is known from determinations of the sign of the e.f.g. at the ^{119}Sn nucleus in the Sn^{II} compounds (which are isoelectronic with Te^{IV} compounds) that the quadrupole interaction is dominated by the extent of p_z character of the non-bonding pair of electrons.[24,25] It seems likely, therefore, that the quadrupole interactions observed in the $^{125}Te^{IV}$ spectra are also dominated by the imbalance in the $5p$ orbital population caused by the stereochemically active non-bonding pair of electrons with substantial p_z character. Since this non-bonding pair of electrons is one of the prime factors leading to the distortion from the regular octahedral environment around Te^{IV} *via* lone-pair–bond-pair repulsions,[26] some correlation between the magnitude of the quadrupole splitting and the type of co-ordination is to be expected. The absence of a general relation between quadrupole splitting and chemical isomer shift (which is essentially constant to within ±0.2 mm s^{-1} for the Te^{IV} compounds studied) also parallels the behaviour of Sn^{II} compounds.[25]

EXPERIMENTAL

Materials.—Authentic samples of MTe_3O_8 (M = Ti, Zr, Hf, or Sn), UTe_3O_9, $NaVTeO_5$, α-$TeVO_4$, β-$TeVO_4$, $V_2Te_2O_9$, $UTeO_5$, $Sc_{0.5}Ta_{0.5}Te_3O_8$, $LiVTeO_5$, $Nb_2Te_2O_9$, and $M_2Te_3O_9$* (M = Al, Cr, or Fe) were kindly supplied by J. Galy, Bordeaux, and authentic samples of Te_2O_5, Te_4O_9, H_2TeO_4, and TeO_3 were kindly made available by J. Moret, Monpellier.

Mössbauer Measurements.—^{125}Te Mössbauer spectra were obtained at 80 K by means of an AM-1 spectrometer (Nuclear Science and Engineering Corp.) incorporating a cryoflask CLF-3 (Texas Instruments Inc.) and an R.I.D.L. 34-128 400-channel analyzer. Both source and absorber were held at 80 K. The ^{125}Te spectra at 4.2 K were recorded using a spectrometer comprising an MVT3 transducer and MD3 drive amplifier and an MFG3 wave-form generator (all from Elscint Ltd.), and an NS 630 multichannel analyzer (Northern Scientific Inc.). Both source and absorber were kept at 4.2 K in an MHC-3 liquid-helium cryostat (Elscint Ltd.) and counts were accumulated in half the 1 024 channels available.

Sources were obtained from the Radiochemical Centre, Amersham. A 10 mCi ^{125}I–Cu source ($t_{\frac{1}{2}}$ 60 d) was used mainly for the work at 80 K and a 20 mCi Zn–^{125m}Te source ($t_{\frac{1}{2}}$ 58 d) for the work at 4.2 K. Comparison of the spectra of (XIX) obtained from both sources indicated that the linewidth Γ was 13% smaller for the Zn–^{125m}Te source. To enhance the flux of the 35.5 keV Mössbauer γ-rays at the detector relative to the far more intense tellurium K X-rays (27.4 and 31.1 keV), a copper foil (0.25 mm thick) was placed in front of the source and the 7 keV Cu X-rays generated in this foil were attenuated by an aluminium absorber (0.5 mm thick) placed in front of the detector.[27,†]

---

* See footnote on p. 2208.

† 1 eV per atom ≈ 96.5 kJ mol^{-1}.

[21] O. Lindqvist, *Acta Chem. Scand.*, 1968, **22**, 977.

[22] L. N. Swink and G. B. Carpenter, *Acta Cryst.*, 1966, **21**, 578.

[23] B. Buss and B. Krebs, *Inorg. Chem.*, 1971, **10**, 2795.

[24] T. C. Gibb, B. A. Goodman, and N. N. Greenwood, *Chem. Comm.*, 1970, 774.

[25] J. D. Donaldson, E. J. Filmore, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1109.

[26] R. J. Gillespie, ' Molecular Geometry,' Van Nostrand Reinhold, London, 1972, p. 42.

[27] C. E. Violet, R. Booth, and F. Wooten, *Phys. Letters*, 1963, **5**, 230; R. Booth and C. E. Violet, *Nuclear Instr. Methods*, 1963, **25**, 1.

Counting was made in conventional transmission geometry using the 6.9 keV escape peak generated by the 35.5 keV γ-rays in an NaI(Tl) crystal (0.13 mm thick). Absorbers consisted of powdered compound (70—185 mg) adjusted so that the absorber thickness was 35 mg Te per cm^2 (*i.e.* 2.5 mg ^{125}Te per cm^2).

The total number of counts per channel was in the range 0.5×10^6—2.3×10^6 after folding to eliminate the geometrical curvature of the base line in the mirror-image spectra. The data were fitted by Lorentzian lines using established computer programs.[28] The velocity scales for the two spectrometers were calibrated by curve fitting the first half of the mirror-image spectrum of ^{57}Fe metal. Zero velocity was also determined by measuring a BaSnO$_3$ absorber against a Ba^{119m}SnO$_3$ source. The chemical isomer shifts of (XIX) at 80 K relative to the Zn–^{125m}Te and ^{125}I–Cu sources both also at 80 K were $-1.10(2)$ and $-1.22(4)$ mm s^{-1}. Accordingly, the values of δ for (XVII) and (XVIII) at 80 K quoted in Table 1 with respect to ^{125}I–Cu were calculated by subtracting 0.12 mm s^{-1} from the experimental data obtained with Zn–^{125m}Te. The same factor was used to convert the observed chemical isomer shifts of absorbers at 4.2 K (relative to the Zn–^{125m}Te source at 4.2 K) into values relative to the ^{125}I–Cu source at 80 K as quoted in Table 2, since δ (Te metal) at 4.2 K was $+0.63(2)$ mm s^{-1} against the Zn–^{125m}Te source at 4.2 K whereas δ (Te metal) at 4.8 K is $+0.51(4)$ mm s^{-1} against a ^{125}I–Cu source at 82 K.[6]

We thank Dr. T. C. Gibb for his advice on the computer analysis of the data, Dr. R. Greatrex for his assistance with the experiments at 4.2 K, the S.R.C. for support, and the Japan Society for the Promotion of Science for the award of a fellowship (to M. T.).

[5/449 *Received, 6th March,* 1975]

---

[28] B. J. Duke and T. C. Gibb, *J. Chem. Soc. (A)*, 1967, 1478.