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^{125}Te Mössbauer Spectra of the Te (*IV*) Oxides and Oxyfluorides

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The ^{125}Te Mössbauer spectra for a number of Te(*IV*) oxides are reported in which the tellurium is present in either a distorted trigonal bipyramidal or distorted tetrahedral coordination with the lone-pair occupying one of the coordinate positions. The isomer shifts and quadrupole splittings are interpreted in terms of the relative *s* and *p* character of the stereochemically active lone-pair. Mössbauer data for $KTeF_5$, $K_2TeO_2F_2$, $Cs_2TeO_2F_2$, and Cs_2TeOF_4 are also presented and discussed.

Introduction

In the past several papers have appeared in the literature in which ^{125}Te Mössbauer data for tellurium oxides and oxyanions have been reported (*1*, *2*, *3*). However, little attempt was made in those works to interpret the results in any detail. In recent years a number of X-ray crystal structures have been reported for the tellurium oxides and it is now apparent that the coordination about tellurium can vary quite widely in these compounds. In the light of this observation the present work was initiated and we report data for eight Te(*IV*) oxides which have not previously been studied, in addition to examining the interpretation of the results for the Te(*IV*) oxides in general.

Recently Milne and Moffet (*4*) have reported the synthesis, ir and Raman data for compounds of the type $M_2TeO_2F_2$ and M_2TeOF_4. We report the Mössbauer data for $K_2TeO_2F_2$, $Cs_2TeO_2F_2$ and Cs_2TeOF_4 and examine the significance of the results for these compounds together with those for K_2TeF_5.

Experimental

The compounds were prepared and characterized using the procedures described in Ref. (*4–15*) and using naturally isotopically abundant tellurium. The Mössbauer spectra were recorded with the source and absorbers at 80°K using an NSEC AM-1 drive coupled to a Nuclear Data 1024 channel analyzer. A dual input multiscaler allowed the accumulation of an ^{57}Fe iron foil calibration spectrum on the rear end of the drive at the same time as the ^{125}Te spectra were recorded. A Ge/Li semiconductor detector was used to monitor the 35.5 keV ^{125}Te Mössbauer γ ray. Absorbers containing ca. 8 mg cm^{-2} ^{125}Te were used and the source was a 10 mCi ^{125}I/Cu source purchased from New England Nuclear. The 512 channel mirror image spectra were folded and computer fitted to Lorentzians using a program originally obtained from Dr. A. J. Stone (*16*). A typical spectrum is shown in Fig. 1.

Results

The Mössbauer data for the compounds investigated are reported in Table I. The available crystallographic data for these compounds are summarized in Table II.

The compounds TeO_2, $Te_2O_4 \cdot HNO_3$, $CuTeO_3$ and compounds containing the TeF_5^- ion have previously been studied by other workers and the results reported here are in reasonable agreement with those results (*3*). It may be noted that Erickson and Maddock (*2*) have commented on the considerable

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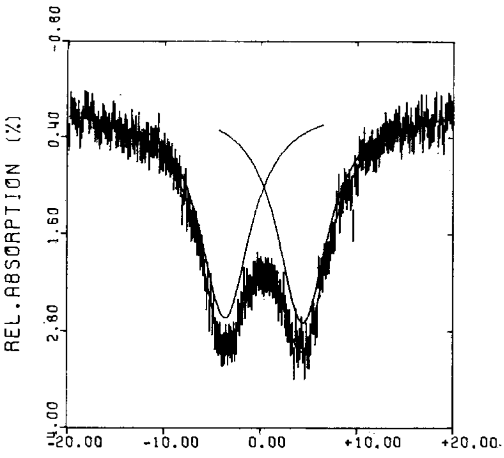

FIG. 1. ^{125}Te Mössbauer spectrum of Cs_2TeOF_4.

discrepancies in ^{125}Te isomer shifts reported by different laboratories. The values relative to ^{125}I/Cu reported by Gibb et al. (*1*), for example, show a marked shift to more positive values in comparison with those generally reported elsewhere. In addition, the quadrupole splittings Δ reported in the literature (*3*) for TeO_2 range from 6.25 to 7.76 mm sec^{-1}, and for Na_2TeO_3 from 5.94 to 6.6 mm sec^{-1}, although the errors on the measurements are often reported to be of the order of ±0.1 mm sec^{-1} or less. These discrepancies may well arise from difficulties inherent in calibrating the spectrometer at the relatively high velocities used in ^{125}Te studies.

Discussion

It is apparent from a cursory examination of Table I that the isomer shifts and quadrupole splittings for the Te(*IV*) oxides each span only a very small range of values.

In compounds one to four of Table I, the tellurium is present in a distorted trigonal bipyramidal environment (Fig. 2) in which it

TABLE I

MOSSBAUER DATA

	δ^{*a}, mm s^{-1} (±0.08)	$\delta\ddagger^{b}$, mm s^{-1}	Δ, mm s^{-1} (±0.2)	$\Delta\ddagger$, mm s^{-1}	Γ, mm s^{-1}
α-TeO_2	+0.78		6.1		7.2
		+0.91 (*12*)		6.25 (*3*)	
		+0.72 (*7*)		6.54 (*12*)	
$Te_2O_4 \cdot HNO_3$	+0.54		5.9		
		+1.4 (*4*)		6.0 (*5*)	6.0
		+0.89 (*19*)		6.65 (*6*)	
$Te(C_6H_4O_2)_2$	+0.69		6.2		6.3
$SnTe_3O_8$	+0.74		7.0		10.2
UTe_3O_9	+0.63		6.7		5.8
$Ni_2Te_3O_8$	+0.68		6.5		6.4
$Mg_2Te_3O_8$	+0.51		7.2		6.1
$CuTe_2O_5$	+0.55		6.6		6.1
$CuTeO_3$	+0.53		5.9		6.4
		+0.37 (*28*)		6.45 (*15*)	
α-$VTeO_4$	+0.37		6.0		6.5
β-$VTeO_4$	+0.46		7.1		6.6
$KTeF_5$	+0.75		6.6		7.1
NH_4TeF_5		+1.09 (*33*)		6.25 (*16*)	
$K_2TeO_2F_2$	+0.45		6.6		6.8
$Cs_2TeO_2F_2$	+0.34		7.4		6.1
Cs_2TeOF_4	+0.71		9.5		7.2

[a] With respect to I/Cu, source and absorber both at 80°K.

[b] $\delta\ddagger$ and $\Delta\ddagger$ values taken from (*3*, pp. 454–5).

TABLE II

CRYSTALLOGRAPHIC DATA

		Bond lengths		Bond angles (degrees)	
	Reference	Equatorial	Axial	O_{ax}–Te–O_{ax} [or O_{ax}–Te–O_{eq}]	O_{eq}–Te–O_{eq}
αTeO_2	(*5*)	2.07 (×2)	1.88 (×2)	168.0	100.6
$Te_2O_4 \cdot HNO_3$	(*6*)	2.02	1.88	147.8	100.0
		2.16	1.95		
$Te(C_6H_4O_2)_2$	(*7*)	2.01	1.98 (×2)	154.3	98.1
		2.11			
$SnTe_3O_8$	(*8*)	2.12 (×2)	1.85 (×2)	156.8	102.9
UTe_3O_9	(*9*)	2.15	1.78	156.6	95.8
		2.16	2.02		
$CuTe_2O_5$	(*10*)	1.92 (×1)	1.87	[92.8	94.6
			1.88	91.0]	
$CuTeO_3$	(*11*)	Te_1 1.86 (×1)	1.89 (×2)	[95.6]	92.7
		Te_2 1.96	1.88 (×2)	176.3	105.7
		2.32			
α-$VTeO_4$	(*12*)	1.99 (×1)	1.81	[92.0	94.0
			1.95	98.5]	
β-$VTeO_4$	(*13*)	2.02	1.85	147.0	95.0
		2.20	1.87		

is bonded to four oxygen atoms and a stereochemically active lone-pair is assumed to occupy the fifth coordinate position in the equatorial plane (Table II). Andersson et al. (*14*) have examined the crystal structure data for a number of oxides, fluorides and oxyfluorides of Sb(*III*), Te(*IV*), and Pb(*II*) and have proposed a simple model for calculating the bond lengths and bond angles in these compounds. They have proposed that the distorted *tbp* geometry arises through hexagonal closest packing of the two axial oxygens with the two equatorial oxygens and the lone-pair. They assume that the distance between the center of the volume of the lone-pair and the cation is ~1 Å, and that this results in the cation being somewhat off center in the equatorial plane, leading to the observed distortion from 180° of the O_{ax}–Te–O_{ax} bond angle (*14*).

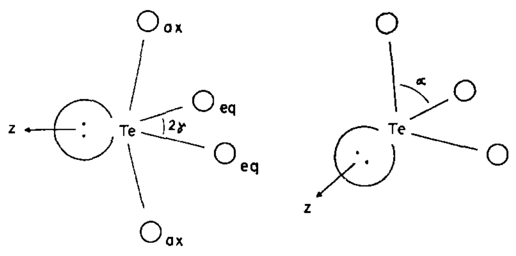

FIGURE 2

In terms of hybrid orbitals the bonding may be described by sp^2 hybridization in the equatorial plane with the lone-pair occupying one of these orbitals and *pd* hybridization in the axial direction. Alternatively, the two axial bonds may be viewed as being formed through a three-center four-electron bond employing only one *p*-orbital on the tellurium. Lone-pair bond-pair repulsions would then lead to the observed distortion of the trigonal bipyramid. Such models are obviously an extreme picture and the hybridization in the plane need not be sp^2 but simply some admixture of *s*, *p* orbitals in which the lone-pair may have significantly more *s*-character and significantly less *p*-character than that required in sp^2 hybridization.

In $CuTe_2O_5$ and α-$VTeO_4$ and for one of the tellurium sites in $CuTeO_3$, the tellurium is found bonded in a pyramidal unit in which the O–Te–O bond angles are all somewhat greater than 90°. Again the lone-pair would appear to be stereochemically active and would now lie along the 3-fold axis, completing a distorted tetrahedron about the tellurium. In hybrid terms the extreme picture would be sp^3 although again the lone-pair would be expected on the basis of the bond angles to have much greater *s*-character than the sp^3 description would imply. Detailed crystal structures of $Mg_2Te_3O_8$ and $Ni_2Te_3O_8$ have not been reported although preliminary studies suggest that these compounds have a structure similar to that of $Sn_2Te_3O_8$ (*15*). In β-$VTeO_4$ and $U_2Te_3O_9$ the coordination about the tellurium appears to be intermediate between that of a distorted tbp and a distorted tetrahedron.

In the above models for the Te(*IV*) oxides it is implicit that the lone-pair is stereochemically active. Since the Mössbauer isomer shift δ reflects the *s*-electron density within the nuclear volume, $|\Psi_s(O)|^2$, δ should reflect the degree to which the 5*s* electrons are incorporated into the bonding orbitals. For ^{125}Te $\Delta R/R$, the nuclear radius term, is positive in sign and therefore the larger $|\Psi_s(O)|^2$ the more positive the isomer shift. The removal of tellurium 5*p* electrons in bonding will lead to an increase in $|\Psi_s(O)|^2$ through deshielding effects, and hence, to a more positive isomer shift, while the incorporation of 5*s* electrons into bonding orbitals will directly decrease $|\Psi_s(O)|^2$ and lead to more negative isomer shifts.

Since Mössbauer isomer shifts can only be considered on a relative scale, Fig. 3 shows the isomer shifts for some representative compounds of Te(*II*) and Te(*IV*). For the octahedral ions TeX_6^{2-} (X = Cl, Br, I), it is generally considered that the $5s^2$ electrons are nonbonding and that the tellurium bonds to the halogen primarily through 3-center 4-electron bonds utilizing the tellurium 5*p* orbitals. Then as the electronegativity of the ligand increases, the effective number of 5*p* electrons removed from the tellurium increases and the isomer shifts become more positive. Similarly in the Te(*II*) thiourea derivatives the 5*s* electrons appear to be stereochemically inert and the tellurium utilizes only its 5*p* orbitals in bonding. In comparison with these compounds, the Te(*IV*) oxides have remarkably small isomer shifts. This immediately suggests that the tellurium 5*s* electrons are participating in the bonding to some extent. In Mössbauer studies of Sn(*IV*) compounds it has been shown that the order of ligand electron withdrawing power for oxygen and the halogens lies in the series F > O > Cl > Br > I, simply reflecting electronegativities (*3*), and on this basis the Te(*IV*) oxides would have been expected to have isomer shifts greater than those of the Te(*IV*) halide derivatives. The trend observed for the Te(*IV*) isomer shifts is similar to that observed for Sn(*II*) and Sb(*III*) where the oxides exhibit much smaller $|\Psi_s(0)|^2$ values than the halide derivatives (*3*). In all three cases the central atom possesses a lone-pair and it is apparent that in the oxides there must be some *s*-bonding character,

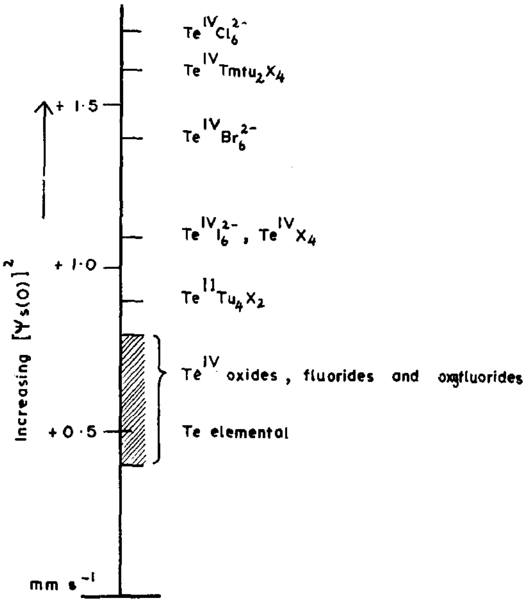

FIG. 3. Isomer shift scale for ^{125}Te, with δ values taken from (*17*), where Tmtu = *tetramethylthiourea* and Tu = *thiourea*.

If it is assumed that in the absence of 5*s* bonding character, TeO_2 would have had an isomer shift comparable with that of $TeCl_6^{2-}$ (+1.7 mm sec^{-1}), then it is possible to estimate the % *s*-character in the bonds. It has previously been concluded that the ^{125}Te isomer shift increases by ca. + 0.4 mm sec^{-1} for each 5*p* electron removed (*17*) and, extrapolating from ^{129}I Mössbauer data (*3*), the removal of one $5s$ electron may then be expected to change the isomer shift by ca. –2.4 mm sec^{-1}. Thus for the Te(*IV*) oxides ca. 9% s-character would be required to produce the observed isomer shifts, and the tellurium would have the approximate electronic configuration $5s^{1.6}$ $5p^{1.9}$, i.e., the effective charge on the tellurium would be ca. + 2.5. As will be discussed below such a configuration is consistent with the interpretation of the quadrupole splittings, and also with the interpretation of the data for TeF_5^- which is isoelectronic with IF_5.

The origin of the quadrupole splittings in the Te(*IV*) oxides are of some interest. In the light of the above discussion, it would appear that the lone-pair on tellurium in these compounds will have significant p-character and it might be anticipated that the lone-pair will contribute to the electrostatic field gradient. However, other possible contributions to the efg must also be considered.

The pyramidal TeO_3 unit observed in $CuTe_2O_5$ and α-$VTeO_4$ is similar to that observed in a large number of Sn(*II*) compounds (*18*), in Sb_2O_3 and the Sb(*III*) halides (*19*), in the $TeCl_3^+$ ion found in $TeCl_4$ (*20*), and even in the IO_3^- ion (*21*), in all cases the central atom possessing a lone-pair. It was proposed by Donaldson and Senior (*18*) that for Sn(*II*) compounds an asymmetrical p-occupation of the *bonding* orbital rather than the p-character of the lone-pair was primarily responsible for the efg. However it has been demonstrated that in SnF_2, V_{zz} is in fact negative, suggesting that it is indeed the p_z-character of the lone-pair which is dominant (*3*). Moreover in the Sb(*III*) compounds (*19*) noted and also in the IO_3^- ion (*22*), V_{zz} is negative in sign, again leading to the same conclusion. For the Te(*IV*) oxides the sign of the efg has not been measured directly. However the ^{129}I Mössbauer emission spectrum of $^{129}TeO_2$ (*23*) shows the iodine to be present in the same lattice environment as the parent tellurium and in that instance the sign of V_{zz} is again negative.

The fact that the quadrupole splittings of tellurium in the different oxides are essentially the same bears further examination. Several models have been used to describe the efg in molecules (*24*), namely the Townes and Dailey theory (*25*), the point charge or additivity model and a simple M.O. description (*26*). The latter melds Lucken's approach (*25*) to the Townes and Dailey theory with the additivity model. Indeed, it is possible to generate all the features of the additivity model starting with the Townes and Dailey theory and simply making the additional assumption that a given *M–X* bond exhibits a constant bond ionicity from one molecule to another within an isostructural series in which the *M–X* bond occupies the same position (e.g., axial). In the present case it seems fitting to return to the Townes and Daley theory and to adopt Lucken's formulation.

We have in the Townes and Dailey theory

$$e^2qQ/e^2qQ_o = -Up = +Uz - (Ux + Uy/2)$$

where Up is the p orbital imbalance, the U terms are the $5p$ orbital populations, e^2qQ is the coupling constant for the molecule of interest and e^2qQ_o is that for one $5p$ hole. For ^{125}Te $e^2qQ_o \sim 24$ mm sec^{-1}. For the tbp geometry, with the lone-pair in the equatorial plane defining the z-axis (*25*),

$$Up = -2(1 - \cot^2\gamma) + a^{tbe}\,(\tfrac{1}{2} - \cot^2\gamma) + a^{tba}/2 \tag{1}$$

$$\eta = |a^{tbe} - a^{tba}|/[2(1 - \cot^2\gamma) + a^{tbe}\cot^2\gamma] \tag{2}$$

where 2γ is the O_{eq}–Te–O_{eq} bond angle and the a terms are the orbital populations in the axial and equatorial directions.

If $2\gamma = 120°$, i.e., the geometry is a regular tbp;

$$Up = -4/3 + a^{tbe}/6 + a^{tba}/2, \tag{3}$$

$$\eta = 3|a^{tbe} - a^{tba}|/(4 + a^{tbe}). \tag{4}$$

For the tetrahedral geometry.

$$Up = [-3\cos\alpha/(1 - \cos\alpha)]\,(a^{tet} - 2) \tag{5}$$

$$\eta = 0, \tag{6}$$

and if the O–Te–O bond angle α is 109.5°,

$$Up = 1.5 + 0.75\,a^{tet} \tag{7}$$

From Eq. (3) and Eq. (7), which are of course analogous to the equations obtained in the point charge model (*24*), it is clear that for these idealized geometries if $a^{tbe} \sim a^{tba} \sim a^{tet}$, then the coupling constants and hence the quadrupole splittings in the two cases would be very similar, as is experimentally observed.

In the analysis of the quadrupole splitting data for Sn(*IV*) compounds, Clark et al. (*26*) found that for distorted molecules inclusion of the angular term $-3\cos\alpha/(1-\cos\alpha)$ gave poorer agreement with the additivity model than the assumption of regular tetrahedral geometry. Indeed, Lucken (*25*) has observed that the sensitivity of the angular term presents a quite general problem in the interpretation of coupling constants derived from nqr data. However, for illustrative purposes we may use Eqs. (1) and (5) to interpret the coupling constants. Thus if all the a terms have a value of ca. 0.5 estimated on the basis of the isomer shift data as discussed above, then the observed quadrupole splittings of ca. 6 mm $\sec^{-1}$, corresponding to $e^2qQ \sim 12$ mm $\sec^{-1}$ and $Up = -0.5$ (assuming V_{zz} is negative), correspond in the tbp case to $2\gamma \sim 102°$ and in the tetrahedral case to $\alpha = 97°$. These angles are in surprisingly reasonable agreement with the experimentally observed values (Table II).

It must be emphasized that the above is only considered a qualitative rationalization of the isomer shifts and quadrupole splittings. Thus, any analysis incorporating the Townes and Dailey theory necessarily assumes that e^2qQ_o is a constant for a given isotope, although it presumably varies with charge, and that the angular dependence of e^2qQ is satisfactorily described in terms of the above equations, although this is often not the case. (*25*). The point-charge model is also dependent on these same assumptions (*26*). The use of isomer shifts to estimate orbital populations is also fraught with danger since the precise dependence of δ on the number of holes in the s and p orbitals can only be estimated by indirect means. Another important point in the present case that has not been discussed above is the probable presence of $O_{p\pi} \rightarrow Te_{d\pi}$ bonding and the influence this will have on δ and Δ. It has been tacitly assumed that d-orbital electrons will not significantly influence either parameter, as is generally assumed for ^{119}Sn, ^{121}Sb, ^{125}Te, and ^{129}I.

With the above provisos in mind the analyses of δ and Δ appear to be reasonably consistent and suggest the presence of ca. 10% s-character in the bonding orbitals. This is significantly less than the 25% implied in the structural model assumed by Andersson *et al.* in discussing these compounds.

$KTeF_5$ and the Oxyfluorides

The spectrum of the TeF_5^- ion has previously been reported by Gibb *et al.* (*1*), and the present data are in reasonable agreement with that work, noting the difference in the isomer shift scales. The TeF_5^- corresponds to a p-orbital imbalance, $Up = e^2qQ/e^2qQ_o$, of ca. 0.5, since $e^2qQ_o \sim 12$ mm $\sec^{-1}$. This is essentially the same as that reported (*27*) for IF_5 ($Up = 0.47$), consistent with a similar structure and a similar p-orbital population in the two cases. For IF_5 the isomer shift and quadrupole coupling constant have been interpreted in terms of the 5s and 5p orbital populations, using data for IF_7 to provide an estimate of the I–F σ-bond orbital population (*27*). It was concluded that in IF_5 the iodine had an effective charge of +4.58, having lost 5.08p electrons from the closed shell $5p^6$ configuration and 0.5s electrons. For TeF_5^-, presumably a similar condition holds with a high effective charge on the tellurium and the presence of some 10% bonding s-character. Thus the isomer shift of TeF_5^- is again relatively small for Te(*IV*) consistent with such s-character in the bonds, while the quadrupole splitting reflects the p-character of the lone-pair and V_{zz} would be negative as in IF_5. Not too surprisingly, the picture here would appear to be similar to that of the Te(*IV*) oxides.

The ir and Raman data for the Te(*IV*) oxyfluorides have been reported by Milne and Moffett (*4*) and the proposed structures are shown in Fig. 4.

Assuming for simplicity that structures (*a*) and (*c*) are regular octahedra and that the bonding can be described as sp^3d^2, and that structure (*b*) is a regular tbp with sp^3d hybridization, then the values of Up predicted by the Townes and Dailey theory are as shown. Here a_O and a_F are the Te–O and Te–F bonding orbital populations respectively, and

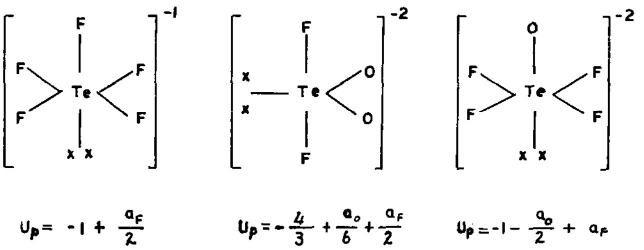

FIG. 4. Proposed structures of the oxyfluorides and that for the TeF_5^- ion. The *Up* values are the *p*-orbital imbalances in the Townes and Dailey theory.

bond ionicities in the octahedral and tbp geometries are assumed to be the same for a given ligand. On the basis of electronegativity differences we would expect $a_O > a_F$. Indeed, in IF_5 $a_F < 0.1$, whereas on the basis of the above discussion a_O in the Te(*IV*) compounds would appear to be ca. 0.5. The simple hybrid models would then suggest that the coupling constants would lie in the order (*a*) < (*b*) ~ (*c*), whereas experimentally it is observed that (*a*) $\lesssim$ (*b*) < (*c*). Moreover, the above models would imply quadrupole splittings, i.e., Δ values, of $\gtrsim 12$ mm sec^{-1}, corresponding to $Up \gtrsim 1$, whereas the observed values are ca. 6–9 mm sec^{-1}. This simply reflects the fact that the simple hybrid schemes overemphasize the role of the 5*s* electrons in bonding and the lone-pair must have considerably more *s*-character than these models would suggest. This of course is consistent with the small positive isomer shifts observed. The trend in the observed quadrupole splittings suggests that the lone-pair must have greater *p*-character in (*c*) than in (*a*) and (*b*). The isomer shift for (*c*) however appears to be more positive than (*b*) presumably reflecting the fact that the fluorines remove more electrons (of predominantly *p*-character) from the tellurium than oxygen.

Conclusions

The general features of the isomer shifts and quadrupole splittings for the tellurium (*IV*) oxides and oxyfluorides can be explained in terms of ca. 10% *s*-character in the bonding orbitals. No attempt has been made to interpret the small differences in the isomer shifts for the oxides, since these differences are comparable with the errors of the measurements. The relatively small isomer shifts together with the coupling constants observed are consistent with significant stereochemical activity of the lone pair, and this is in general agreement with the crystal structures of these compounds, where known. A description of the bonding in these compounds in terms of sp^3, sp^3d and sp^3d^2 hybrids, however, would appear to overemphasize the role of the *s*-electrons in bonding.

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