Tellurium-125 Mössbauer Spectra of some Aryltellurium-(II) and -(IV) Compounds

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^{125}Te Mössbauer parameters are reported for a number of aryltellurium-(II) and -(IV) compounds: RTeX, R_2Te, R_2Te_2, $RTeX_3$, and R_2TeX_2 (R = Ph, p-MeC_6H_4, p-$MeOC_6H_4$, or p-$EtOC_6H_4$; X = Cl, Br, or I).

THE Mössbauer effect for ^{125}Te has been known for 12 years.[1] Greenwood and Gibb [2] reviewed the literature in 1971. More recently, Jones and his co-workers discussed Mössbauer parameters of tellurium(IV) halides,[3] hexahalogenotellurates(IV),[3] and thiourea complexes [4,5] of tellurium-(II) and -(IV). ^{125}Te Mössbauer investigations of some aryl derivatives of tellurium-(II) and -(IV) are reported here.

RESULTS AND DISCUSSION

The results are summarised in the Table. The quantity $\Delta R/R$ is positive for tellurium,[6] so large positive values of δ correspond to high *s*-electron density at the nucleus.

Chemical isomer shifts, quadrupole splittings, and linewidths for the aryltellurium compounds at 4·2 K

Compound	M.p. (θ_c/°C)	Source	δ(I–Cu) / mm s^{-1}	Δ / mm s^{-1}	2Γ / mm s^{-1}
(p-$PhOC_6H_4)_2Te_2$	87—88	PbTe	0·3	10·3	6·9
(p-$MeOC_6H_4)_2Te_2$	56	PbTe	0·3	10·3	6·5
(p-$MeOC_6H_4)_2Te$	52—53	PbTe	0·3	11·3	6·7
PhTeI	224—227	I–Cu	0·6	9·5	11·7
(p-$MeC_6H_4)_2Te_2$	51—52	I–Cu	0·6	9·9	11·5
(p-$MeC_6H_4)_2Te$	63—64	I–Cu	0·7	10·1	10·9
(p-$EtOC_6H_4)_2TeCl_2$	109	PbTe	0·7	9·1	6·4
Ph_2TeCl_2	157·5—159	PbTe	0·5	9·2	6·6
Ph_2TeBr_2	203·5—204	PbTe	0·5	8·1	7·4
Ph_2TeI_2	226—229	I–Cu	0·7	5·9	6·3
(p-$MeC_6H_4)_2TeCl_2$	161—163·5	I–Cu	1·6	8·1	12·4
(p-$MeC_6H_4)_2TeI_2$	210—212	PbTe	0·6	6·3	6·5
(p-$MeOC_6H_4)TeCl_3$	198	PbTe	0·9	9·2	7·4
(p-$EtOC_6H_4)TeCl_3$	187	PbTe	1·1	9·2	6·9
(p-$EtOC_6H_4)TeBr_3$	187—190	PbTe	1·0	8·0	6·9
(p-$EtOC_6H_4)TeI_3$	144—146	PbTe	1·0	5·2	7·1
$PhTeI_3$	168—175	I–Cu	0·9	3·9	8·4

Aryltellurium(II) *Derivatives.*—The tellurium(II) compounds in the Table form two distinct groups: (*a*) *p*-phenoxy- and *p*-methoxy-phenyl derivatives which have low chemical isomer shifts, δ 0·3 mm s^{-1}, and high quadrupole splittings, Δ 11·3—10·3 mm s^{-1}; and (*b*) phenyl and *p*-tolyl derivatives which have intermediate chemical isomer shifts, δ 0·6—0·7 mm s^{-1}, and fairly high quadrupole splittings, Δ 10·1—9·5 mm s^{-1}. The chemical isomer shifts and quadrupole splittings are lower than for square-planar thiourea complexes of Te^{II}.[4] Quadrupole splittings for the aryltellurium(II) compounds are higher than for the aryltellurium(IV) compounds.

Crystal-structure determinations show that simple aryltellurium(II) compounds are covalent molecules with bond angles in the range expected for sp^3 or p^3 hybridised tellurium, *e.g.* (p-$MeC_6H_4)_2Te$ (101·0 ± 2·7°) [7] and (p-$ClC_6H_4)_2Te_2$ (94·4°).[8] It would be interesting to discover whether the presence of oxygen reduces the stereochemical activity of the non-bonding electrons, either by intramolecular electronic effects or by intermolecular association in the solid state.

Diaryltellurium(IV) *Dihalides.*—The chemical isomer shifts of all the diaryltellurium dihalides except (p-$MeC_6H_4)_2TeCl_2$ are within the range δ 0·5—0·7 mm s^{-1}. The only other organotellurium compound whose Mössbauer spectrum has been reported [9] is (covalent) α-Me_2TeI_2, δ 0·55 mm s^{-1}. The chemical isomer shifts of the diphenyl derivatives are less for the chloride than the iodide, which is opposite to the trend in hexahalogenotellurates(IV).[3,10] The quadrupole splittings, Δ 9·2—5·9 mm s^{-1}, decrease in the order chlorides > bromides > iodides, which is consistent with decreasing stereochemical activity of the non-bonding electrons and increasing symmetry with increasing size of halide.

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The crystal structures of Me_2TeCl_2,[11] Ph_2TeBr_2,[12] and α-Me_2TeI_2[13] are similar, and have been described as distorted tetrahedral, distorted trigonal bipyramidal, and distorted octahedral, depending on the significance attributed to intermolecular attractions and the mixing of *p*-electron density with the 5*s* electrons. Low-frequency i.r. and Raman spectra of many diaryltellurium dihalides are consistent with ψ-trigonal-bipyramidal structures.[14]

The high chemical isomer shift of $(p\text{-}MeC_6H_4)_2TeCl_2$, δ 1·6 mm s^{-1}, is within the range observed for octahedral complexes of Te^{IV} [3,4,10] and if confirmed would suggest a different type of structure, *cf.* β-Me_2TeI_2 which consists of $[Me_3Te]^+$ and $[MeTeI_4]^-$ ions linked by iodine bridges so that the tellurium atoms are in distorted octahedral environments.[15]

Aryltellurium(IV) *Trihalides*.—The chemical isomer shifts of the aryltellurium trihalides, δ 0·9—1·1 mm s^{-1}, are higher than those of the diaryltellurium dihalides and close to the values for tellurium(IV) halides.[3] The quadrupole splittings, Δ 9·2—3·9 mm s^{-1}, decrease markedly in the order chlorides > bromides > iodides, indicating increasing electronic symmetry with increasing size of halide. There is spectroscopic evidence that aryltellurium trihalides are associated in the solid state.[16]

EXPERIMENTAL

The aryltellurium compounds were prepared by standard methods. The Mössbauer sources were ^{125}I in a copper matrix and $Pb^{125m}Te$ (which gave better spectra) at 4·2 K. The results were fitted to two lines and are quoted to 0·1 mm s^{-1}. No attempt was made to reproduce these values with different samples of compounds. Great significance should not be attached to small numerical differences, because the linewidths of the Mössbauer transitions were relatively large. Chemical isomer shifts are with respect to ^{125}I–Cu, using the relation (1).[17]

$$\delta(^{125}I\text{–}Cu) = \delta(Pb^{125m}Te) + 0{\cdot}15 \text{ mm s}^{-1} \qquad (1)$$

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