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A MÖSSBAUER SPECTROSCOPIC INTERPRETATION OF SOME PROPERTIES OF ORGANOTELLURIUM COMPOUNDS

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Summary

A review of Tellurium-125 Mössbauer parameters is used to explain the colour of some organotellurium compounds in terms of the population of low energy conductance bands by non bonding electrons.

Introduction

The sign of $\Delta R/R$ is positive for the ^{125}Te transition [1] and consequently more positive chemical isomer shifts may be correlated with higher s-electron densities at the tellurium nucleus. Removal of 5p electrons in the formation of chemical bonds deshields, and thereby increases, the tellurium s electron density at the nucleus, whilst the direct removal of 5s electrons decreases the s-electron density. The quadrupole splitting of

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some organotellurium compounds have been rationalised in terms of an additivity model based on the Townes and Dailey Theory [2,3]. Large quadrupole splittings have been associated with considerable tellurium 5p orbital population imbalence [2,3].

It has been suggested that colour may be caused by the overlap of orbitals of intermolecularly associated heavy atoms [4,5]. ^{119}Sn Mössbauer isomer shift data and the colours of caesium tin(II) bromides have been interpreted in terms of the direct population of $5s^2$ non bonding electrons of conductance bands formed by overlap of empty p or d orbitals of the co-ordinated atoms [6].

Discussion

Organotellurium Mössbauer parameters are given in Table 1.

Tellurium(II) derivatives

The chemical isomer shifts of the diaryl tellurides are smaller and the quadrupole splittings larger than the values recorded for elemental tellurium. The C-Te-C bond angle [10] of 101.0 ± 2.7° in $(p\text{-}CH_3C_6H_4)_2Te$ and the small chemical isomer shift are consistent with significant stereochemical activity of the 5s electrons. The more positive chemical isomer shifts of the ditellurides indicate less s-character in the Te-Te bond than in the Te-C bond and are consistent with the smaller C-Te-C bond angle [11] of 94° in $(p\text{-}ClC_6H_4)_2Te_2$.

With the exception of $(C_6H_5)_2Te$ which is yellow, the diaryl tellurides are colourless. The crystal structure [10] of $(p\text{-}CH_3C_6H_4)_2Te$ shows it to exist as discrete molecules in which tellurium atoms are more than 6Å apart. Pale yellow cyclic organic compounds of tellurium(II) [5,12] have been shown to involve intermolecular tellurium associations greater than 5Å in length and bright yellow organic cyclic tellurium(II) derivatives [13] appear to have similar tellurium polymeric associations of *ca.* 4Å.

Table 1

^{125}Te Mössbauer Data and Colours of some Organotellurium Compounds.

Compound	Colour	$\delta \pm 0.10$ mms^{-1} (I/Cu)	$\Delta \pm 0.1$ mms^{-1}	Reference
Tellurides				
$(CH_3)_2Te$	White	0.06	10.5	2
$(C_6H_5)_2Te$	Yellow	0.18	10.5	2
$(p\text{-}CH_3OC_6H_4)_2Te$	White	0.3	11.3	7
$(p\text{-}CH_3C_6H_4)_2Te$	White	0.7	10.1	7
Ditellurides				
$(C_6H_5)_2Te_2$	Red	0.37	10.7	2
$(p\text{-}CH_3OC_6H_4)_2Te_2$	Dark red	0.42	10.1	2,7
$(p\text{-}C_2H_5OC_6H_4)_2Te_2$	Orange	0.28	10.6	2
$(p\text{-}C_6H_5OC_6H_4)_2Te_2$	Red brown	0.32	10.0	2,7
$(p\text{-}CH_3C_6H_4)_2Te_2$	Orange	0.6	9.9	7
$C_2H_4Te_4$	Black	0.27	9.33	9
Fluorides				
$(C_6H_5)_2TeF_2$	White	0.52	10.4	3
$(p\text{-}C_2H_5OC_6H_4)_2TeF_2$	White	0.36	10.1	3
$(p\text{-}CH_3OC_6H_4)_2TeF_2$	White	0.54	10.0	3
$(p\text{-}CH_3OC_6H_4)TeF_3$	White	0.56	8.6	3
$(p\text{-}C_2H_5OC_6H_4)TeF_3$	White	0.60	8.6	3
Chlorides				
$(CH_3)_2TeCl_2$	White	0.58	9.4	2,8
$(C_6H_5)_2TeCl_2$	White	0.5	9.2	7
$(p\text{-}CH_3OC_6H_4)_2TeCl_2$	White	0.68	9.1	2,3
$(p\text{-}C_2H_5OC_6H_4)_2TeCl_2$	White	0.7	9.1	7
$(p\text{-}C_2H_5OC_6H_4)TeCl_3$	Yellow	0.91	9.4	2,7
$(p\text{-}CH_3OC_6H_4)TeCl_3$	Yellow	0.9	9.2	7

(continued)

Table 1 (continued)

Bromides				
$(CH_3)_2TeBr_2$	Yellow	0.65	8.5	2,8
$(C_6H_5)_2TeBr_2$	Yellow	0.6	7.9	2,7
$(\underline{p}\text{-}CH_3OC_6H_4)_2TeBr_2$	Yellow	0.72	7.8	3
$(\underline{p}\text{-}C_2H_5OC_6H_4)_2TeBr_2$	Yellow	0.52	7.6	2
$C_6H_5TeBr_3$	Yellow	0.91	7.8	2
$(\underline{p}\text{-}C_2H_5OC_6H_4)TeBr_3$	Yellow	1.0	8.0	7
Iodides				
$(CH_3)_2TeI_2$	Violet	0.52	7.6	2,8
$(\underline{p}\text{-}CH_3C_6H_4)_2TeI_2$	Red Brown	0.6	6.3	7
$(\underline{p}\text{-}CH_3OC_6H_4)_2TeI_2$	Red Brown	0.51	6.1	3
$(C_6H_5)(CH_3)TeI_2$	Red	0.56	6.4	3
$(C_6H_5)_2(CH_3)TeI$	White	0.38	5.6	3
$(C_6H_5)(CH_3)_2TeI$	Yellow	0.32	5.4	3
$(\underline{p}\text{-}C_2H_5OC_6H_4)TeI_3$	Brown	1.0	5.2	7

It is suggested here that the involvement of intermolecular tellurium associations in addition to short Te-C and Te-Te bonds gives rise to highly coloured diaryl ditellurides as shown by red polymeric $(C_6H_5)_2Te_2$ in which the Te-Te bond is 2.7Å and the intermolecular contacts are 4.2Å [14]. The tellurium atoms in diorgano ditellurides therefore have a higher degree of co-ordination than those in the tellurides as a result of both intra- and inter- molecular bonding. The donation and movement of non-bonding valence electrons into the conductance band formed by overlap of the empty orbitals on the atoms gives rise to the orange, red or brown colours characteristic of these compounds.

Tellurium(IV)

The description of $(CH_3)_2TeCl_2$[15], $(C_6H_5)_2TeBr_2$[16] and α-$(CH_3)_2TeI_2$ [17], as distorted tetrahedral, distorted trigonal bipyramidal and distorted octahedral depend on the significances attributed to intermolecular attractions through bridging halogens and the mixing of *s* with *p* electrons. The dichlorides, dibromides and diiodides have, on the basis of low frequency infrared and Raman spectroscopy, been conviently described as ψ-trigonal bipyramids in which the halogens occupy the axial positions [18] . The quadrupole splittings increase in the order I<Br<Cl<F and reflect the decreasing occupation of the tellurium $5p_z$ orbital.

The chemical isomer shifts of the diaryltellurium(IV) dihalides are more positive than those of the organotellurium(II) compounds and reflect the deshielding of the *5s* electrons from the tellurium nucleus which results from the withdrawal of *5p* electrons by the halogens. It is difficult to asseys the variation of electron density at the tellurium nucleus with increasing electronegativity of halogen because of the large errors involved with the determination of the isomer shift, the variation of *s* - *p* hybrid character of the bonds as in organotin(IV) halides, and the reported isomer shift increase of only 0.4 mms^{-1} for the removal of one tellurium *5p* electron [19]. It has, however, been suggested that the smaller chemical isomer shifts of the colourless diaryltellurium(IV) difluorides indicate a greater involvement of the stereochemically active lone pair in an unassociated structure [3].

The diorganotellurium(IV) - dichlorides are white, the -dibromides are yellow and the -diiodides are violet or dark red. It is suggested here that as in the case of the highly coloured ditellurides the increasing intensification of colour with increasing atomic weight of the halide is a result of the intra- and inter- molecular associations between adjacent tellurium and heavy halogen atoms. Crystallographic studies of the two dark violet compounds (p-$ClC_6H_4)_2TeI_2$ [20] and 1-thia-4-telluracyclohexane 4,4-diiodide [21] have shown them to involve extensive tellurium - iodine and secondary iodine - iodine intermolecular bonding. In contrast, red 1-oxa 4- telluracyclohexane 4,4-diiodide [22] and phenoxtellurium 10,10-diiodide [4] involve only tellurium-iodine intermolecular bonds. Yellow 1-thia-4, telluracyclohexane 4,4-dibromide [23] contains tellurium - bromine intramolecular bonds of 2.65Å and inter-molecular associations of 3.59Å in addition to intermolecular tellurium - sulphur associations of 3.58Å. Organic solutions of molecular diorganotellurium(IV) diiodides are yellow or orange suggesting that the unassociated molecules are yellow and that intermolecular association in the solid state causes a shift in colour to red or violet. It appears that the coloured organotellurium(IV) compounds are those involving extensive intermolecular associations through heavy halogen atoms and small distances between those atoms forming the conductance bands. The population of these bands by $5s^2$ non bonding electrons gives rise to colour as in bromine compounds of tin(II) [6]. The quadrupole splittings for the diorganotellurium(IV) diiodides are smaller than those of the other diorganotellurium(IV) dihalides reflecting the higher degree of co-ordination and symmetry of the tellurium atom. The chemical isomer shifts are smaller than those in the dibromides and suggest enhanced donation of tellurium electron density into the band formed with the iodine orbitals. The trioganotellurium(IV) iodides are yellow or white which suggest little or no intermolecular association. X-ray, infrared and conductance studies on R_3SeCl and R_3TeX [24-27] suggest that the compounds contain the R_3Te^+ cation.

Spectroscopic evidence suggests that the aryltellurium(IV) -trichlorides, -tribromides and -triiodides are associated in the solid state [28]. The chemical isomer shifts are more positive than those for the corresponding dihalides suggesting enhanced halogen removal of tellurium 5p electrons whilst the quadrupole splittings are comparable implying similar modes of bonding. The anomolous quadrupole splittings for the trifluorides have been attributed to the presence of a different environment about the tellurium atom [3] and may not be unexpected given the structural differences known to exist between TeF_4 and $TeCl_4$ or TeI_4 and between SbF_3 and the other Sb(III) halides. The white colour of the trifluorides compared with the yellow or brown colours characteristic of the other trihalides [28] supports this speculation of a significantly different structure.

The diaryltellurium(IV) dicarboxylates are colourless. Their ^{125}Te Mössbauer parameters [3] are similar to those of the-dichlorides and -difluorides and support their infrared structural assignments as unassociated ψ-trigonal bipyramids [29].

The black colour of cyclic $C_2H_4Te_4$ indicates a large degree of both intra- and inter- molecular tellurium bonding. The low chemical isomer shift implies significant donation of s- electron density into the conductance bands.

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