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A ^{125}Te Mössbauer Study of Tellurium Compounds Containing Thiourea Derivatives

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The Mössbauer and structural data for tellurium compounds containing thiourea derivatives have been rationalized by Jones *et al.* [1–5] in terms of the Foss bonding scheme. According to this scheme four electrons in two independent non-bonding lone-pairs with either 5s or 5p character are present in the tellurium(II) compounds, together with two mutually orthogonal three-centre molecular orbitals, each formed by a 5p-tellurium orbital and the σ-orbitals of two ligand atoms. Because of the presence of the pure 5s and 5p non-bonding orbitals, the Foss model is unable to explain the observed distortions in the square-planar tellurium(II) site and the spread of the isomer shift values.

An improvement of the Foss model has been recently proposed [6]. It requires a hybridization between the 5s and all the 5p tellurium orbitals, which are energetically similar. In this way, two sets of hybrid orbitals are formed: one is composed of two symmetrical, non-bonding, sp_z lone-pair hybrids normal to the bonding plane, and the other by the sp_x and sp_y hybrids. This model could explain the distortions from ideal square-planar geometry and the rather large differences of the isomer shifts. In this note, the Mössbauer parameters of a number of square-planar tellurium(II) and octahedral tellurium(IV) compounds are discussed within this framework.

Results and Discussion

The compounds were prepared by adapting literature methods [7–9] and characterized by elemental analysis and infrared spectroscopy. Analytical data for the compounds not previously reported are listed in Table I.

The Mössbauer parameters for the square-planar tellurium(II) compounds of Table II are characterized by a positive isomer shift S, and a large electric quadrupole splitting ΔE_Q. Linewidths 2Γ close to the minimum observable width of 5.14 mm/s were obtained with a source of ^{125}Sb in Rh and absorbers containing about 1.5 mg ^{125}Te/cm^2. Both source and absorber were kept at 4.2 K; a sinusoidal velocity waveform was employed and an intrinsic Ge detector was used to detect the 35.5 keV rays. Isomer shift data from the literature were converted to the reference system of the Sb(Rh) source, by using either the values given in ref. 10 or the present isomer shift at 4.2 K of ZnTe, 0.099(5) mm/s. Square-planar tellurium(II) compounds exhibit a single quadrupole doublet. A second doublet observed for Te(dmtu)$_4$-

TABLE I. Analytical Data for the New Compounds.[a]

	M.p.[c]	Analysis (%)[b]				$\Delta\nu$(CS)[d]	$\Delta\nu$(CN)[d]
		C	H	N	X		
Te(dchtu)$_4$F$_2$	146	57.2(55.4)	8.6(8.6)	10.1 (9.9)		−17	+26
Te(dphtu)$_2$Cl$_2$	134	47.3(47.7)	3.7(3.7)	8.3 (8.5)	11.2(10.8)	−9	+22
Te(diptu)$_2$Cl$_2$	164	32.4(32.1)	6.8(6.9)	10.8(10.7)	13.4(13.5)	−7	+23
Te(dchtu)$_2$Cl$_2$	153	45.6(46.0)	7.1(7.1)	7.9 (8.2)	10.7(10.4)	−15	+36
Te(dchtu)$_2$I$_2$	192	35.6(36.2)	5.4(5.6)	6.3 (6.5)	29.0(29.4)	−12	+18
Te(dchtu)(NCS)$_2$[e]	112	38.1(37.2)	4.9(5.0)	11.9(11.6)		−12	+20
$\{(EtHN)_2CS\}_2\cdot TeBr_6$		14.1(13.8)	2.7(2.8)	6.8 (6.4)	56.8(55.0)	−6	+54
$\{(H_2N)_2CS\}_2\cdot TeCl_6$		5.0 (4.9)	1.3(1.2)	11.5(11.4)	4.8 (4.9)	−2	+64

[a] dchtu = 1,3-dicyclohexylthiourea; dphtu = 1,3-diphenylthiourea; diptu = 1,3-diisopropylthiourea. [b] Calculated values are in parentheses. [c] Melting points were determined under vacuum, in °C. [d] Infrared shift from the uncoordinated thourea-type ligand, in cm^{-1}. [e] The thiocyanate group is N-bonded: ν_{CN} = 2053, ν_{CS} = 814, and δ_{NCS} = 486 cm^{-1} (ref. 18).

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TABLE II. Mössbauer Parameters for Square-Planar Tellurium(II) Compounds at 4.2 K.[a]

	$S^{b,c}$	$\Delta E_Q{}^c$	$2\Gamma_{av}{}^c$
1. $Te(dmtu)_4Cl_2$	0.91(5)	17.65(9)	5.6(1)
2. $Te(tu)_4Cl_2 \cdot 2H_2O$	1.04(5)	15.83(9)	5.5(1)
3. $Te(tu)_4(ClO_4)_2{}^d$	0.96(5)	16.5(2)	7.4(3)
4. *cis*-$Te(tu)_2Cl_2$	0.89(5)	15.35(9)	5.5(1)
5. $Te(dphtu)_2Cl_2$	0.89(5)	15.97(9)	5.6(1)
6. $Te(diptu)_2Cl_2$	0.96(5)	12.24(9)	5.6(1)
7. $Te(dchtu)_2Cl_2$	0.93(5)	15.87(9)	5.5(1)
8. $Te(dchtu)_2I_2$	0.98(5)	16.02(9)	5.6(1)
9. *trans*-$Te(tmtu)_2Cl_2$	1.08(5)	17.60(9)	5.4(1)
10. $Te(tu)_3(HF_2)_2$	1.05(5)	15.51(9)	5.5(1)
11. $Te(dchtu)(NCS)_2$	1.08(5)	15.47(9)	5.7(1)

[a] dmtu = 1,3-dimethylthiourea; tu = thiourea. [b] With respect to $^{125}Sb(Rh)$ source. [c] In mm/s. [d] From ref. 6 at 80 K.

Cl_2 and $Te(dchtu)(NCS)_2$ can be attributed to a partial decomposition.

The isomer shift for tellurium(II) compounds (Table II) is relatively large, but less positive than that for the tellurium(IV) compounds (Table III), in which the removal of the $5p_z$ electrons reduces the shielding of the 5s electrons from the nucleus.

The small isomer shift range of the monomeric square-planar compounds (1–3 of Table II) containing the $TeL_4{}^{2+}$ ion [6, 11, 12], like the isomer shift data previously reported [2, 3], point to a small 5s character in the Te–S bonds. These bonds are weakly covalent, with bond lengths larger than the sum of the covalent single bond radii of 2.41 Å and with S–Te–S bond angles not far from 90°.

From the available crystallographic data [13–15] the tellurium atom lies in the centre of symmetry of the square-planar $TeL_4{}^{2+}$ entities in the *trans* TeS_2X_2 isomers and on the twofold symmetry axis in the *cis*-isomers. In both isomers, however, the tellurium coordination geometry is far from the ideal one. The deviations indicate a large 5s character in the bonding plane for both the *cis* and the *trans* isomers involving sp_x and sp_y hybrids, which tend to make the isomer shift more negative.

On average the isomer shift values decrease on going from the square-planar compounds of Table II containing the ionic moiety TeS_4 to the *cis* or *trans* TeS_2X_2 isomers. In every case, however, the planar geometry is maintained. This is observed even in $Te(tu)_3(HF_2)_2$ for which X-ray data reveal a binuclear cation based on a four-coordinated tellurium(II) atom with a distorted square-planar coordination geometry [16], while the present Mössbauer spectrum shows that the two tellurium sites are equivalent.

TABLE III. Mössbauer Parameters for Octahedral Tellurium(IV) Compounds at 4.2 K.

	$S^{a,b}$	$\Delta E_Q{}^b$	$2\Gamma^b$
1. $\{(Me_2N)_2CS\}_2 \cdot TeCl_6$	1.59(5)	0	6.0(3)
2. $\{(EtHN)_2CS\}_2 \cdot TeBr_6$	1.58(5)	0	6.2(1)
3. $\{(H_2N)_2CS\}_2 \cdot TeCl_6$	1.80(5)	0	5.9(1)
4. *trans*-$Te(tmtu)_2Cl_4{}^c$	1.56(6)	0	9.5
5. *trans*-$Te(tmtu)_2Cl_4{}^d$	1.48(7)	0	8.6
6. *trans*-$Te(tmtu)_2Br_4$	1.67(5)	0	7.4(1)

[a] With respect to $^{125}Sb(Rh)$ source. [b] In mm/s. [c] Orthorhombic form from ref. 2. [d] Monoclinic form from ref. 4.

The decrease of the isomer shift values (Table II) reveals an increase in the sp_x and sp_y hybrid formation. In this way, the 5s character of these tellurium hybrids is altered, but not the 5p character, in agreement with the large, nearly constant quadrupole splittings of Table II and of other similar compounds previously reported [2, 3]. The large quadrupole coupling at the tellurium nucleus is generated from a 5p electron imbalance between the equally occupied p_x and p_y orbitals and the p_z orbital, whence V_{zz} is expected to have a negative sign. Similar splittings point to a similar p-electron imbalance, but not necessarily to the same coordination geometry. This is inferred from the data of Table II, where the tellurium coordination varies from strongly distorted *cis* or *trans* square planar in TeS_2X_2 to but slightly distorted square-planar in TeS_4. Also $Te(dchtu)(NCS)_2$, whose tellurium site is probably similar to the one found in $Te(tmtu)Cl_2$ [17] has a quadrupole splitting similar to $Te(tu)_3(HF_2)_2$.

The presence of two symmetrical sp_z orbitals above and below the coordination plane prevents a close approach of anions from both the sides of the xy-plane in the square-planar tellurium(II) compounds containing the $TeL_4{}^{2+}$ ions. The available crystal structures suggest the presence of a strong electrostatic repulsion along this direction. Therefore, the electrostatic effect of such anions should contribute little to the quadrupole interaction. This means that the splitting for the square-planar tellurium(II) compounds and (in particular) for compounds 1–3 is entirely due to the 5p electron imbalance in the bonding plane and is independent of the apical anion.

The Mössbauer parameters for the tellurium(IV) compounds listed in Table III arise from the presence of three mutually orthogonal three-centre bonds and a stereochemically inactive 5s lone-pair [19]. Other than for the lone-pair distorted compounds containing the isoelectronic tin(II) and antimony(III) ions, a regular octahedral geometry is expected for these tellurium(IV) compounds [20].

Unfortunately a direct comparison of structural and Mössbauer data among isoelectronic and isostructural compounds containing the same thiourea derivatives is impossible because very few examples of tin(II) [21] and antimony [22] compounds are known.

The first three compounds in Table III consist of TeX_6^{2-} anions and $\{(R_1R_2N)_2CS\}_2^{2+}$ cations, with $R_1 = R_2 = Me$; $R_1 = Et$, $R_2 = H$; $R_1 = R_2 = H$. These cations result from two thiourea-type molecules connected by an S–S single bond [9]. A single, unsplit narrow Mössbauer line has been obtained for $\{(Me_2N)_2CS\}_2 \cdot TeCl_6$, in agreement with the undistorted octahedral symmetry for the $TeCl_6^{2-}$ anion found by its X-ray crystal structure determination [23]. In a similar way a narrow, unsplit Mössbauer line is observed for $\{(H_2N)_2CS\}_2 \cdot TeCl_6$ and $\{(EtNH)_2CS\}_2 \cdot TeBr_6$. While structural data are not available for $\{(EtHN)_2CS\}_2 \cdot TeBr_6$ the crystal structures for $\{(R_1HN)_2CS\}_2 \cdot TeCl_6$, R_1 = Me or Et, are known [9, 24] and they show that the environment of the tellurium centre is influenced by an asymmetric net of hydrogen bonds connecting the chlorine atoms to the amidic nitrogens. The distortion is remarkable because the Cl–Te–Cl bond angle deviates from the ideal value by as much as 5° while the Te–Cl bond length ranges from 2.4 to 2.7 Å.

The observation of an essentially unsplit line with merely a small broadening in $Te(tmtu)_2Br_4$ as well as the correspondent chlorine compounds (Table III) would appear astonishing because of the deviation from the octahedral symmetry in these compounds [25, 26], which would suggest a substantial electric quadrupole splitting. An explanation of this finding may be that the p-electron population in the p_x, p_y and p_z orbitals is altogether very small since these are filled only by covalency effects. The quadrupole splitting thus merely gives rise to the broadening of the lines whose widths are the largest in Tables III and II. In the same way, the compounds 1–3 of Table III appear undistorted within the limits of detection of the ^{125}Te Mössbauer resonance.

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