Bond Lengths in Square-Planar Tellurium(II) Complexes

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Crystal structure determinations [1] of square-planar tellurium(II) complexes [2-6] have led to the following values for tellurium-ligand bond lengths; the uncertainties quoted are estimated standard deviations.

Tetrathiourea-tellurium(II) dichloride dihydrate [1a,2,3], Te(tu)$_4$Cl$_2$.2H$_2$O: Te—S = 2.68 ± 0.01 Å.

Tetrathiourea-tellurium(II) dichloride [1b,3], Te(tu)$_4$Cl$_2$: Te—S = 2.69 ± 0.01 Å.

trans-Dimethanethiosulphonato-dithiourea-tellurium(II) [1c,4], Te(tu)$_2$(S$_2$O$_2$CH$_3$)$_2$: Te—S(thiourea) = 2.65 ± 0.015 Å; Te—S(thiosulphonate) = 2.68 ± 0.015 Å.

trans-Dibromobis(ethylenethiourea)tellurium(II) [1d,5], Te(etu)$_2$Br$_2$: Te—S = 2.69 ± 0.015 Å; Te—Br = 2.78 ± 0.01 Å.

The results indicate that, with single covalent bond radii for ligands, a bonding radius of 1.64 Å can be assigned to tellurium(II) in square-planar complexes.

In two *cis* complexes, a marked lengthening effect of a thiourea group on a Te—Cl or Te—Br bond *trans* to it is apparent:

cis-Dichloro-dithiourea-tellurium(II)[1e,2,6], Te(tu)$_2$Cl$_2$: Te—S = 2.48 ± 0.02 Å; Te—Cl = 2.92 ± 0.015 Å.

cis-Dibromo-dithiourea-tellurium(II)[1f,2,6], Te(tu)$_2$Br$_2$: Te—S = 2.47 ± 0.03 Å; Te—Br = 3.05 ± 0.01 Å.

However, the Te—S bonds are correspondingly shorter; the sum of the Te—Br and Te—S bond lengths in *cis*-Te(tu)$_2$Br$_2$ is 5.52 Å as compared with 5.47 Å in *trans*-Te(etu)$_2$Br$_2$. In *cis*-Te(tu)$_2$Cl$_2$ the sum of the Te—Cl and Te—S bond lengths is 5.40 Å whereas two times 1.64 Å for tellurium plus the single bond radii, 0.99 and 1.04 Å of chlorine and sulphur gives 5.31 Å. Thus, even if the two bonds *trans* to each other are fairly unequal in strength, the sum of their lengths shows only a slight increase. Or in other words, the sum of the bonding radii of tellurium(II) in directions at 180° remains fairly constant.

These observations seem to fit the delocalized molecular orbital scheme based on *p*-functions, developed by Pimentel [7], Hach and Rundle [8,9] and Havinga and Wiebenga [10,11] for bonding in polyhalide ions. In a linear trihalide ion one *p*-orbital of the central atom forms two bonds, at 180°. Support for this type of bonding in polyhalide ions has recently come from nuclear quadrupole resonance measurements [12,13] and studies of bond stretching force constants [14]. Similarly in square-planar tellurium(II) complexes, one tellurium 5*p* orbital would bind two ligands, at 180°; increased engagement of the orbital in bonding to one of the ligands would reduce its bonding capacity for the other ligand.

Krebs [15,16] has pointed out that in halfmetals, like tellurium, bonded atoms have nearest non-bonded neighbours in directions approximately linear to the bond. Thus in hexagonal tellurium, an infinite, nearly linear sequence of atoms occurs, with interatomic distances of 2.86, 3.46 and 3.46 Å within the repeat unit; Krebs [15,16] postulates *p*-electron resonance along the chain. It is of interest to note that the average interatomic distance in the chain is two times 1.63 Å.

The extreme asymmetry in strength of two co-linear bonds from an atom, based on one *p*-orbital only of the latter, would be a single covalent bond in one direction and no bond in the other. If the sum of the bonding radii of the atom in the two directions remains constant, the observed "half *p*-bond" radius of 1.64 Å for tellurium(II) would be the average of the single covalent radius, 1.37 Å, and the no-bond radius, *i.e.* the van der Waals radius. This leads to 1.91 Å for the van der Waals radius of tellurium, which is the same as the value, 1.9 Å, given by Briegleb [17]. The slight increase actually observed in the sum of the lengths of the two bonds might then have its cause in an increase in the bonding radius of the more loosely bound ligand; this radius approaches the van der Waals radius, or the ionic radius, as the asymmetry of the complex increases.

For selenium and sulphur, taking as their van der Waals radii about half the shortest non-bonded distances in α-monoclinic [18] and β-monoclinic [19] selenium, 3.53 and 3.48 Å, and in orthorhombic sulphur [20] and cesium hexasulphide [21], 3.37 and 3.39 Å, the above reasoning together with the single covalent radii of 1.17 and 1.04 Å would give about 1.46 and 1.36 Å, respectively, for the "half *p*-bond" radii of divalent selenium and sulphur. Thus, with the radii in the middle column the average of those in the left and right:

	Single covalent	"Half p-bond"	No-bond (v. d. Waals)
Sulphur	1.04 Å	1.36 Å	1.68 Å
Selenium	1.17	1.46	1.75
Tellurium	1.37	1.64	1.91

A linear, symmetrical S—S—S arrangement is present in 2,5-dimethyl-thio-thiophthen [22-25]. The expected S—S bond length in such a sulphur(II) complex would be about 1.36 Å + 1.04 Å = 2.40 Å. The observed bond length [25] is 2.35 Å; however, the S—S bonds are here part of a bicyclic unsaturated system and may be subject to shortening through π-bonding.

The work on tellurium(II) complexes was started with a view towards these as model substances for the transition state in nucleophilic displacements on divalent chalcogens. The results, and also kinetic evidence from displacements on sulphur [26], indicate a linear transition state. Furthermore, the picture emerges that in the linear transition state the in- and out-going groups are bonded, at 180°, through a single p-orbital of the electrophilic centre. This possibility was considered, and preferred, by Fava *et al.*[27,28] on kinetic grounds. Nucleophilic reactivity may then relate to the ability of the reagent to engage the p-orbital in bonding, at the expense of the bond at 180°. Electrophilic reactivity would correspondingly reflect the centre's ability to participate in delocalized p-bonding in the transition state.

It appears likely that π-bonding, superimposed on the delocalized σ p-bonding, may affect the stabilities of complexes as well as the reactivities, and in the case of different ligands in directions at 180°, influence the relative bond lengths in these directions; for example dative π-bonding from central atom $p\pi$ to ligand $d\pi$ as has been discussed for chloroiodides [9] and phosphinesulphide-iodine complexes [29].

1. Work, to be published, by (*a*) K. Fosheim and A. Scheie, (*b*) S. Solheimsnes, (*c*) K. Marøy, (*d*) H. Kjøge, (*e*) K. Johnsen and K. Marøy, (*f*) K. Maartmann-Moe and the author.
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