Preparation of Methyltrihalogeno(tetramethylthiourea)tellurium(IV) Compounds: Pentaco-ordinate Tellurium

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Summary A new class of five co-ordinate, monomeric, tellurium compounds have been prepared.

METHYL-SELENIUM AND -TELLURIUM trihalides have been the subject of recent studies in our laboratory.[1] It was postulated that the chalcogen atom uses mainly *p*-orbitals in bonding leading to a maximum co-ordination number (C.N.) of six, and that an organo-group exhibits a strong "*trans*-bond lengthening" effect severely limiting co-ordination *trans* to that group. This approach led to the prediction that the central atom in organochalcogen trihalides would have a C.N. of five in the solid state achieved through bridging halogens.

This co-ordination theory also has important bearing on the Lewis acid behaviour of chalcogen and organochalcogen-(IV) halides. It predicts that $RTeX_3$ molecules should behave as Lewis acids with one site available for co-ordination by base.† We sought to test this idea by attempting to prepare adducts of organotellurium trihalides with suitable Lewis bases.

Methyltellurium trichloride (16·0 mmole) was suspended in 80 ml benzene. Transfers, filtrations, etc., were carried out in a dry nitrogen atmosphere. Tetramethylthiourea (tmtu) (16·0 mmole) in 20 ml CH_2Cl_2 was added and the mixture was stirred magnetically for 0·5 hr. When the resulting solution was cooled to $-20°$, yellow crystals

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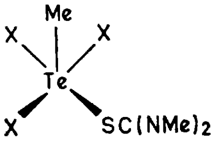
† This approach also rationalizes the formation of $TeX_4\cdot 2B$ (B = thiourea, amines) complexes by tellurium tetrahalides (these adducts are *trans* octahedral species: S. Husebye and J. W. George, *Inorg. Chem.*, 1969, **8**, 313). According to our theory there are two available sites for co-ordination to Te in a TeX_4 molecule.

(5·1 g) formed and were filtered from the solution. Evaporation of the solution gave 0·5 g additional product. Yield 91·4%, m.p. 123—125°: $MeTe_3Cl_3$(tmtu), by analysis and molecular weight. A similar procedure utilizing $MeTeBr_3$ gave yellow-orange crystals of CH_3TeBr_3(tmtu), m 120—122°.

Even when a threefold excess of base was present only 1 : 1 complexes crystallized from solutions containing tmtu $MeTeCl_3$ or $MeTeBr_3$. Both compounds are very soluble in CH_2Cl_2 and $PhNO_2$, moderately soluble in $CHCl_3$, but insoluble in C_6H_6. Molecular weight measurements indicate both adducts are monomeric in $PhNO_2$. In addition, the very strong absorption at 333 cm^{-1} found for $MeTeCl_3$ in C_6H_6 is completely absent in the spectrum of CH_3TeCl_3 (tmtu) in $CHCl_3$ suggesting little, if any, dissociation to $MeTeCl_3$ and tmtu. Two peaks in a 4 : 1 ratio were observed in the ^1H n.m.r. spectrum of both compounds further confirming the $MeTeX_3$(tmtu) stoicheiometry.

For $MeTeX_3$(tmtu) we suggest a square pyramidal structure with the methyl group in the apical position.



The proposed structure parallels that found for the isoelectronic $[MeTeI_4]^-$ ion[2] Our i.r. data also support the above structure. In solid $MeTeCl_3$ the highest Te–Cl frequencies (due to a *cis*-$TeCl_2$ group) are found at 338 and 315 cm^{-1}.[1] In contrast the highest Te–Cl frequency in solid $MeTeCl_3$ (tmtu) is at 251 cm^{-1}. This is quite close to the highest frequency found in Me_2TeCl_2 (277 cm^{-1}).[3] It is therefore suggested that the 251 cm^{-1} absorption in $MeTeCl_3$ (tmtu) is primarily due to trans Cl–Te–Cl stretching. This argument might be questioned as there are *cis*-$TeCl_2$ groups in the suggested structure. Sulphur in thioureas appears to have a stronger *trans*-bond lengthening effect organotellurium(II) halide adducts then does halogen.[4] We suggest a similar lengthening may occur in the above organotellurium(IV) halide complexes to such a degree that only the *trans*-chlorines are involved in the highest Te–Cl frequency. Similar i.r. data were obtained on $MeTeBr_3$ (tmtu). We are starting *X*-ray crystallographic studies to determine the structure of these compounds unambiguously.

Five-co-ordination is rather uncommon in Group VIB. In oxodichlorobis(pyridine)selenium(IV), Se is pentaco-ordinate with *trans*-chlorines and *trans*-pyridines in the base of a square pyramid.[5] Methyltrihalogeno(tetramethylthiourea)tellurium(IV) compounds appear to be the second class of monomeric molecules in which a Group VIB element is pentaco-ordinate.

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[4] O. Foss and S. Husebye, *Acta Chem. Scand.*, 1966, **20**, 132.

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