LIGATION OF SOME SULPHUR DONORS WITH TELLURIUM (II AND IV)

by

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THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS FOR
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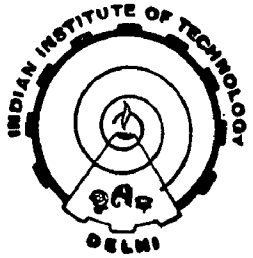

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C E R T I F I C A T E

This is to certify that the thesis entitled "**LIGATION OF SOME SULPHUR DONORS WITH TELLURIUM(II AND IV)**", being submitted by Mr. Jayanta K. Basumatary to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Basumatary has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

A K Singh 22/3/90

(A. K. Singh)
Thesis Supervisor

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ABSTRACT

In the present thesis entitled, "Ligation of Some Sulphur Donors with Tellurium(II and IV)," ligational behaviour of thiosemicarbazones (XTSC) with tellurium(II and IV) has been studied. The complexes of the types $[ArTe(XTSC)_2]Cl$, $Te(XTSC)_2Cl_2$, $Te(XTSC)_4Cl_2$, $TeCl_4.XTSC$, $TeCl_3(XTSC-H)$, $Te_2Cl_7(XTSC-H)$, $ArTeCl_3.XTSC$ and $Ar_2TeCl_2.XTSC$, where XTSC = benzaldehyde, salicylaldehyde, acetophenone and 2-hydroxyacetophenone thiosemicarbazone and Ar = C_6H_5, $4\text{-}HOC_6H_4$, $4\text{-}CH_3H_6H_4$ and $4\text{-}CH_3OC_6H_4$, have been synthesized. Triphenyltellurium(IV) dithiocarbamates (N-methyl, N,N-dimethyl, N,N-diethyl, N,N-diethanol, pyrrolidine and morpholine dithiocarbamates), xanthates (methyl, ethyl, n-propyl, i-propyl, i-butyl and cyclohexyl xanthates) and dithiophosphates (O,O-dimethyl, O,O-diethyl and O,O-diisopropyl dithiophosphates) have also been synthesized. Based on IR, ^1H and ^{13}C NMR spectral data in conjunction with the conductance and molecular weight measurements, the structures of all these new derivatives are proposed.

Three coordinate tellurium(II) complexes of the type $[ArTe(XTSC)_2]Cl$, where Ar = C_6H_5, $4\text{-}HOC_6H_4$ and $4\text{-}CH_3OC_6H_4$, have been synthesized by treating $ArTeCl_3$ with the thiosemicarbazones in aqueous methanol. Molecular weight and conductivity measurements suggest that the chloride in these

complexes is ionic. The IR, ^{1}H and ^{13}C NMR data suggest that the coordination of XTSC is through sulphur alone, probably giving a three coordinate tellurium in $[ArTe(XTSC)_2]^+$, in which Te-S bond appears to be of 3c-4e type. The tellurium(II) complexes of the types $Te(XTSC)_2Cl_2$ and $Te(XTSC)_4Cl_2$ have been isolated by reacting TeO_2 dissolved in concentrated HCl with the thiosemicarbazones. IR, ^{1}H, and ^{13}C NMR spectra of these complexes indicate that XTSC coordinates with tellurium only through sulhpur. Most probably Te-S bond in them is also of three centre-four electron (3c-4e) type. These results exhibit that thiosemicarbazones may ligate with tellurium(II) in a manner parallel to that of thiourea. The square planar arrangement of the ligands around tellurium is proposed for $Te(XTSC)_2Cl_2$ and $Te(XTSC)_4Cl_2$ both. In the latter the two Cl atoms may be present above and below the TeS_4 plane resulting in a highly distorted octahedral geometry around Te.

The reactions of thiosemicarbazones with $TeCl_4$ in benzene give the complexes $TeCl_4$.XTSC, $TeCl_3$(XTSC-H) and Te_2Cl_7(XTSC-H). The structural features of these tellurium derivatives explored by IR, ^{1}H and ^{13}C NMR and conductance measurements, appear to be based on an octahedral arrangement of ligands around tellurium. The presence of <u>fac</u> and <u>mer</u> isomers in equilibrium (in solution) has been indicated in the case of $TeCl_3$(XTSC-H). The complexation

occurs through S, nitrogen of >C=N- group and O^- (if present on the benzene ring). The Te_2Cl_7(XTSC-H) species seem to have chlorine bridged and octahedrally coordinated tellurium atoms. The molecular complexes of the types $ArTeCl_3$.XTSC and Ar_2TeCl_2.XTSC, where Ar = C_6H_5, 4-$CH_3C_6H_4$ and 4-$CH_3OC_6H_4$ have been synthesized by stirring/refluxing $ArTeCl_3/Ar_2TeCl_2$ with XTSC in benzene or toluene. The molecular weight measurements in acetonitrile reveal them to be ionic but due to ion association their conductances have been found to be lower than that of a 1:1 electrolyte. IR, ^1H and ^{13}C NMR spectra indicate that XTSC ligates only through sulphur of thiocarbonyl group and therefore Te appears to be five coordinated in both the types of complexes. A square pyramidal geometry around tellurium is proposed on the basis of infrared data and reported crystal structures of $PhTeCl_3$ and Ph_2TeCl_2.

Ph_3TeCl has been found to react with a molar equivalent of sodium dithiocarbamate, xanthate or dithiophosphate (S-SNa) to give Ph_3Te(S-S) type of derivatives. Molecular weight and conductivity measurements in solution suggest that these new triphenyltelluronium compounds are ionized in polar solvents but show a very strong tendency of ion-association. The IR spectral data suggest that all these sulphur donors are coordinated in the η^1 mode in these compounds. Their ^1H NMR spectra are characteristic, and are

consistent with the monodentate behaviour of the sulphur ligands. Photolysis of their toluene/benzene/chloroform solution (1 to 10 mM) gives Ph_2TeO, biphenyl and disulphide. When O_2 is bubbled through their solutions during photolysis, TeO_2 is also formed. The rate of the UV-promoted decomposition decreases in the order xanthate > dithiocarbamate > dithiophosphate.

C O N T E N T S