PREPARATION AND CHARACTERISATION OF AMINOARYLTELLURIUM TRIHALIDES AND THEIR SALTS

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TO MY BELOVED PARENTS

C E R T I F I C A T E

This is to certify that the thesis entitled " Preparation and Characterisation of Aminoaryltellurium Trihalides and their Salts", being submitted by Mr Ashok Kumar Gupta 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. Gupta 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 thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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A C K N O W L E D G E M E N T S

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(ASHOK KUMAR GUPTA)

A B S T R A C T

A number of review articles have appeared during the last few years covering the literature on organo-tellurium compounds. Many substances reported in literature are poorly characterised and many contradicting statements have been published concerning their reactions. A relatively less work is reported on compounds of the type $RTeX_3$ (where R = alkyl or aryl, X= halogen). The present work has,therefore, been undertaken with a view to prepare some aminoaryltellurium trihalides and their salts and characterise them using conductance and molecular weight measurements, nuclear magnetic resonance, ultraviolet, infrared and mass spectrometric techniques.

The thesis has been divided into five chapters.

The first chapter is a review of literature on various aspects of the chemistry of tellurium(IV) compounds. An attempt has been made to cover the literature on tellurium halides, diorganyltellurium dihalides, organyltellurium trihalides and their salts in such a way so as to bring out discrepancies clearly.

The second chapter deals with the preparation and characterisation of aminoaryltellurium trihalides and bis(amino-aryl)-tellurium dihalides. Aminoaryltellurium tribromides and triiodides have been prepared by two different methods. Three

different methods have been followed for the preparation of bis(aminoaryl) tellurium dibromides, whereas the halogen-exchange reaction method has been followed for the preparation of bis(N,N-dimethylaniline) tellurium diiodide..

Aminoaryltellurium tribromides are all yellow in colour, whereas the triiodides deep violet to black. All these compounds are fairly stable in dry air, but get hydrolysed in the presence of moisture. Hydrolysis studies of these compounds show that while, N,N-dimethylanilinetellurium trichloride and tribromide get hydrolysed as soon as they are put in water, the triiodide hydrolysed only very slowly. The main hydrolysis products are tellurium dioxide, amine hydrogen halide and halogen acid. Their conductance data in acetone, acetonitrile and nitrobenzene indicates that these compounds dissociate in dilute solutions and behave as 1:1 electrolyte presumably by the formation of $ArTeX_2^+$ and X^- ions. Their molecular weight data, however, indicates that the dissociation is very less at higher concentrations(above 10 m mol^{-1}) and the compounds mainly exist in the molecular form. In case of N,N-dimethylanilinetellurium trihalides where the solubility is high the polymeric species are formed.

The structural studies of amincaryltellurium trihalides have been presented in the third chapter. Nuclear magnetic

resonance, ultraviolet, infrared and mass spectroscopic techniques have been used to elucidate the structures of these compounds.

N.m.r.spectra suggest a symmetrical substitution of benzene ring. In all these compounds aromatic protons resonate somewhat to the low field of the corresponding amines and also of benzene. This is explained on the basis of the dissociation of these compounds into $ArTeX_2^+$ and X^- ions as observed by conductance measurements described in chapter 2. The positive charge developed on tellurium leads to deshielding of the ring protons. However, due to the presence of a strong electron donating (amino) group, the aromatic protons do not appear at as low a field as in $C_6H_5TeCl_3$ or $p\text{-}CH_3C_6H_4TeCl_3$. The low field shifts of the aryl protons, in general, increase slightly along the series $ArTeCl_3 < ArTeBr_3 < ArTeI_3$ which has been explained on the basis of Te-X bond strength and their solubility.

Ultraviolet spectra of N,N-dimethylanilinetellurium trihalides have been recorded in methanol and acetonitrile. It is concluded that the halotellurium group decreases the resonance effect in the benzene ring. The solvent effect has been discussed. The methanolic solutions of these compounds show fine structure of the primary band whereas the acetonitrile solution does not. This is explained on the basis of difference in polarity of these two solvents.

Infrared spectra of these compounds have been recorded in the range 4000-70 cm^{-1}. These spectra are quite complex and hence the bands pertaining to $-NR_2$ group, carbon-nitrogen, tellurium-carbon and tellurium -halogen bonds only are discussed.

The position of N-H stretching and bending vibrations in these compounds suggest that the $-NH_2$ or $-NHCH_3$ group remains intact and no Te-N bond is formed.

The far infrared data suggest a dimeric structure, in which tellurium aquires a five coordination through halide bridging in agreement with the theory of Wynne and Pearson. Since the tellurium-halogen bond formed between tellurium and bridging halogen is longer than that formed between tellurium and terminal halogen, a structure based on $ArTeX_2^+$ units associated with halide bridges to give a five coordinate tellurium atom is also suggested.

Mass spectra of N,N-dimethylanilinetellurium trihalides have been discussed and the possible fragmentation schemes suggested. The spectra of all the three compounds show a base peak at m/e = 120, which corresponds to either $C_6H_5N(CH_3) = CH_2^+$ or $C_6H_4N(CH_3)_2^+$ ion. Molecular ion peak is observed only in the spectra of N,N-dimethylanilinetellurium triiodide. The TeX_3^+, TeX_2^+, TeX^+ and Te^+ ions can readily be identified in the mass

spectra of these compounds as they show, in general, the same distribution of masses as is theoretically expected. A metastable peak at m/e = 116 is observed in all the compounds and it has been contributed to the metastable transition of $C_6H_4N(CH_3)_2^+$ (m/e = 120) ion to $C_6H_4N(CH_3)=CH^+$ (m/e = 118) ion in a single step by the loss of a hydrogen molecule.

The fourth chapter includes the preparation and characterisation of tetrahaloaminoaryltellurates(IV). Two methods have been followed for the preparation of these compounds.

The conductance data suggest that these compounds dissociate in dilute solution and the values of molar conductance in most cases lie in between the range for 1:1 and 1:2 electrolytes. This has been explained on the basis of dissociation of these compounds in two steps.

In the first step the compound behaves a 1:1 electrolyte, but subsequently the anion formed also undergoes dissociation and behaves as 1:2 electrolyte. The degree of dissociation of anion increases with dilution and in a number of cases in nitromethane solution a behaviour of 1:2 electrolyte is observed.

The infrared spectra of these compound have been recorded in 4000-70 cm^{-1} region and the results discussed. The compounds prepared by the action of halogen acid on aminoaryl-

tellurium trihalides show the bands characteristic of NH_3^+, NH_2^+ or NH^+ grouping. However, other tetrahalotellurates(IV) show the spectra similar to the corresponding aminoaryltellurium trihalide in the range 4000-400 cm^{-1}.

The far infrared data suggest a square based pyramidal structure with C_{4v} symmetry for $ArTeX_4^-$ species whereas a similar structure with a symmetry lower than C_{4v} for the $ArTeX_3Y^-$ species. However, the structure is to be supported by Raman data.

A resume and further scope of the work is given in the fifth and the last chapter.

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