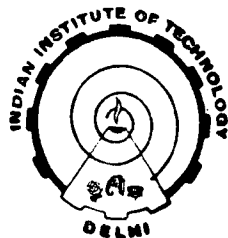


**TELLURIUM (IV) - β - DIKETONATES :
PREPARATIVE AND SPECTRAL INVESTIGATIONS**

*SUBMITTED
IN FULFILMENT OF THE
REQUIREMENTS OF THE DEGREE OF
DOCTOR OF PHILOSOPHY*

By
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TO THE
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
FEBRUARY, 1989

DEDICATED TO

MY

PARENTS

CERTIFICATE

This is to certify that the thesis entitled, "Tellurium(IV)- β -Diketonates: Preparative and Spectral Investigations", being submitted by Mr. Narendra Singh Bhandari, 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. Bhandari has worked under my guidance and supervision and has fulfilled the requirements for the submission of the 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.



15/2/89
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ABSTRACT

In the thesis entitled "Tellurium(IV)- β -Diketonates: Preparative and Spectral Investigations", organotellurium(IV) derivatives of acetylacetone (acacH), benzoylacetone (bzacH), dibenzoylmethane (dbmH), theonyltrifluoroacetone (ttaH), trifluoroacetylacetone (tfacH), trifluorobenzoylacetone (btfacH), 4-acetyl-3-methyl-1-phenylpyrazol-5-one (AMPPH), 4-trifluoroacetyl-3-methyl-1-phenylpyrazol-5-one (TFMPPH), 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (BMPPH) and 4-(3,5-dinitrobenzoyl)-3-methyl-1-phenylpyrazol-5-one (DMPPH) have been described.

The compounds of the type Ph_3TeL , (where $\text{L} = \beta$ -diketonate or pyrazolonate anion) and Ph_2TeL_2 (where $\text{L} = \beta$ -diketonate anion) were prepared by reacting triphenyltellurium(IV) chloride and diphenyltellurium(IV) chloride with sodium salts of β -diketonates and pyrazolonates in 1:2 (aqueous solution) and 1:2.5 (dry benzene) molar ratio. Compounds of the type $\text{Ph}_n\text{TeCl}_{3-n} (\text{C}_5\text{H}_6\text{O}_2) \text{HgCl}$ ($n = 0, 2$ and 3) were synthesized by the reaction of 3,3-bis(chloromercury)pentane-2,4-dione with equimolar amounts of $\text{TeCl}_4/\text{Ph}_2\text{TeCl}_2$ in dioxane and Ph_3TeCl in methanol. The reaction of ArTeCl_3 [where $\text{Ar} = \text{C}_6\text{H}_5$, 4- HOC_6H_4 , 4- $\text{CHO}_6\text{C}_6\text{H}_4$, 4- $\text{C}_2\text{H}_5\text{OC}_6\text{H}_3$, 3- CH_3 -4- HOC_6H_3 and 3,4- $(\text{OH})_2\text{C}_6\text{H}_3$)] with

acetylacetone (acacH) in dry benzene resulted ArTe $(\text{CH}_2\text{COCH}_2\text{COCH}_3)\text{Cl}_2$.

On the basis of molecular weight and conductance measurements and spectral data (IR, Far IR, ^1H , ^{13}C and ^{199}Hg NMR and mass) following conclusions have been drawn:

- (i) In Ph_3TeL type compounds the β -diketonate group is bonded to Te via one oxygen atom. The ionic character of Te-O bond depends on the nature of β -diketonate group. The ion association is very high for pyrazolonates and low for fluorinated β -diketonates.
- (ii) β -diketonate anions asymmetrically ligate with Te in Ph_2TeL_2 resulting in a distorted octahedral environment of ligands around it.
- (iii) In $\text{Ph}_n\text{TeCl}_{3-n}(\text{C}_5\text{H}_6\text{O}_2)\text{HgCl}$ (where $n = 0, 2, 3$) type compounds tellurium moiety is linked with C_3 -carbon of acetylacetone and there is an appreciable Hg-O secondary interaction.
- (iv) The tellurium moiety is linked to C_1 -carbon of acetylacetone in compounds of the type ArTe $(\text{CH}_2\text{COCH}_2\text{COCH}_3)\text{Cl}_2$. These compounds show keto-enol tautomerism in solid state as well as in solution. Tellurium seems to be weakly interacting with oxygen of carbonyl group in them.

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