International Journal of Research
Available at https://edupediapublications.org/journals
p-ISSN: 2348-6848
e-ISSN: 2348-795X
Volume 03 Issue 01
January 2016

Investigation of tellurium Complexes Containing bidentate Schiff Base Derived from Vanillin and 4-Aminoantipyrine

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Abstract: A novel bidentate Schiff base derived from vanillin and 4-aminoantipyrine, form 1:1 complexes with aryltellurium(IV) trichlorides and diaryltellurium(IV) dichlorides of the type VL-AAP.$ArTeCl_3$ and VL-AAP.Ar_2TeCl_2 (where Ar = *p*-methoxyphenyl, *p*-ethoxyphenyl, *p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl and VL-AAP = Schiff base). These complexes have been characterized by elemental analyses, molar conductance, IR and ^1H NMR spectroscopy. On the basis of these studies the donor sites have been identified as carbonyl oxygen of the pyrazolone ring and nitrogen atom of azomethine group (CH=N) to give five membered chelate ring with tellurium centre having *Ψ*-octahedral geometry. The synthesized ligand, and its aryltellurium complexes were screened for their antimicrobial activity against various bacterial and fungal strains.

Keywords: Vanillin, 4-Aminoantipyrine, Aryltellurium(IV), Diaryltellurium(IV), Antimicrobial activity.

Introduction

In last few decades, there has been a considerable interest in the chemistry of antipyrine and its derivative due to their potential biological activity[1] as analgesic[2,3] and anti-inflammatory[3], antiviral[4,5], antibacterial[4,5] and anticancer activity[6].

Among the various derivatives, 4-aminoantipyrine form a variety of Schiff bases with aldehydes/ketones and are reported to be effective ligands having biological and clinical applications[7-9].

The ligands contain antipyrine skeleton in their structure having the hetroatoms in the ring[10] which induces the biological activity[11-13]. The carbonyl group in the base is a potential donor due to large dipole moment[14] (5.48 D) and strong basic character.

Also, aryltellurium(IV) chlorides are known to act as Lewis acids[15-31] and form complexes with several N- , O- and S-donor bases. As a part of our continuing interest on the synthesis of potential bioactive compounds, we hereby report the synthesis, characterization and biological studies on aryltellurium(IV) trichlorides, $ArTeCl_3$ and diaryltellurium(IV) dichlorides, Ar_2TeCl_2 complexes with Schiff base derived from 4-aminoantipyrine and vanillin.

Experimental

All preparations were carried out under an atmosphere of dry nitrogen and the solvents used were purified by standard method[32,33] before use. The purity of compounds was checked by TLC using Silica gel-G (Merck). Melting points were determined in open capillary tube and are uncorrected.

Carbon, hydrogen and nitrogen analyses were obtained microanalytically from SAIF, Panjab University Chandigarh on a ThermoFinnigan CHNS analyser. Conductivity was measured in DMSO at 25±2 ˚C with dip type conductivity cell on a microprocessor based conductivity bridge type MICROSIL.

Infrared Spectra(4000-400 cm^{-1}) were recorded in KBr pellets on a F.T. Infra-Red Spectrophotometer Model RZX (Perkin Elmer) at SAIF, Panjab University Chandigarh. Proton Magnetic Resonance Spectra were recorded in DMSO-d_6 using Tetra methyl silane as an internal reference on BRUKER AVANCE II 400 NMR spectrometer. The antimicrobial activity was evaluated by tube dilution method at Department of Pharmaceutical Sciences, M. D. University, Rohtak.

Preparation of Aryltellurium(IV) Trichlorides and Diaryltellurium(IV) Dichlorides

p-Methoxyphenyltellurium(IV) trichloride[34,35], bis(*p*-methoxyphenyl)tellurium(IV) dichloride[35,36], *p*-ethoxyphenyltellurium (IV) trichloride[37], bis(*p*-ethoxyphenyl)tellurium dichloride[37] *p*-hydroxyphenyltellurium(IV) trichloride[38], bis(*p*-hydroxyphenyl) tellurium(IV) dichloride[38], 3-methyl-4-hydroxyphenyltellurium(IV) trichloride[39] and bis(3-methyl-4-hydroxyphenyl) tellurium(IV) dichloride[39] were prepared by the reactions of $TeCl_4$ with anisole, phenetole, phenol, *o*-cresol respectively, by the methods reported in the literature[34-39].

Preparation of Vanillin-4-aminoantipyrine Schiff base (VL-AAP)[40]

Equimolar amounts of saturated methanolic solution of vanillin and 4-aminoantipyrine were mixed thoroughly and few drops of glacial acetic acid was added. The mixture was refluxed for 4 hours at 70-80˚C on a water bath. The resulting solution was cooled at room temperature, and then poured into crushed ice with constant stirring. The sodium bisulphite solution was added to the precipitate to remove excess aldehyde if any. The crystalline product was dried under vacuum and kept in desiccator over P_4O_{10} until further use. Yield = 90 %, M.pt.= 165-167 ˚C. Analysis (Calculated) $C_{19}H_{19}N_3O_3$: C(67.66), H(5.68) and N(12.46); Found: C(67.50), H(5.82) and N(12.27)

Preparation of Schiff Base Complexes of Aryltellurium (IV) Trichlorides and Diaryltellurium(IV) Dichlorides

Aryltellurium(IV) trichlorides, $ArTeCl_3$ and diaryltellurium(IV) dichlorides Ar_2TeCl_2 (Ar = *p*-methoxyphenyl, *p*-ethoxyphenyl, *p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl), when reacted with VL-AAP in equimolar ratio, yield VL-AAP.$ArTeCl_3$ and VL-AAP.Ar_2TeCl_2 type complexes.

A saturated methanolic solution of 2 mmol of aryltellurium(IV) trichloride or

diaryltellurium(IV) dichloride was added dropwise to the suspension of 2 mmol Schiff base in 60 mL benzene + 40 mL methanol. The reaction mixture was further refluxed for 3-4 hours, cooled and filtered off to remove any turbidity. The filtrate was then concentrated to about one third of original volume under reduced pressure and cooled in an ice bath to obtain coloured product. This was filtered, washed with benzene + methanol (1:1) and dried in vacuum desiccator over P_4O_{10}.

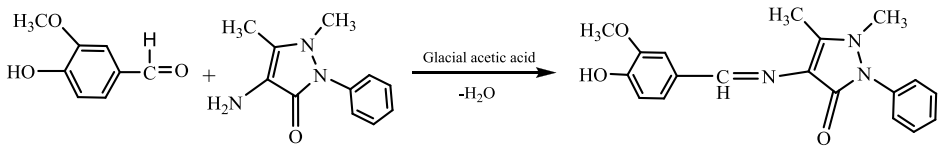
Results and Discussion

$TeCl_4$ when heated with anisole[34-36], phenetole[37], phenol[38], *o*-cresol[39] (Ar-H) appears to undergo Friedel-Crafts type condensation reaction whereby $TeCl_3^+$ unit attacks a position *para* to the alkoxy/hydroxyl groups in the aromatic rings, thus resulting in the formation of aryltellurium(IV) trichlorides and diaryltellurium(IV) dichlorides.

$$Ar\text{-}H + TeCl_4 \longrightarrow ArTeCl_3 + HCl$$

$$2\ Ar\text{-}H + TeCl_4 \longrightarrow Ar_2TeCl_2 + 2\ HCl$$

Formation of Schiff base (VL-AAP) by the reaction of vanillin drug and 4-aminoantipyrine can be represented by following equations.



Vanillin 4-aminoantipyrine Schiff base(VL-AAP)

Schiff base (VL-AAP) reacts with aryltellurium (IV) trichlorides and diaryltellurium(IV) dichlorides in 1:1 molar ratio to yield the corresponding aryltellurium(IV) complexes.

$$\text{VL-AAP} + \text{ArTeCl}_3 \longrightarrow (\text{VL-AAP}).\text{ArTeCl}_3$$

$$\text{VL-AAP} + \text{Ar}_2\text{TeCl}_2 \longrightarrow (\text{VL-AAP}).\text{Ar}_2\text{TeCl}_2$$

All the tellurium(IV) complexes are coloured, crystalline solids, stable at room temperature and non-hygroscopic in nature. The complexes have been analyzed for their tellurium, chlorine, carbon, hydrogen and nitrogen contents and the data along with their physical properties and yields.

Conductance Studies

Molar conductance (Λ_M) data for the complexes at *ca.* 10^{-3} M in DMSO lie in the range 12.41-25.22 S cm^2 mol^{-1}, which predict the non electrolyte[41,42] type behaviour of these complexes in DMSO.

Infrared Spectra

The spectra of VL-AAP Schiff base complexes are quite complex and an attempt has therefore been made to identify the donor sites by comparing the spectra of complexes with parent ligand and $ArTeCl_3$/Ar_2TeCl_2.

In IR spectrum of ligand shows intense band at 1621 cm^{-1} ascribed to carbonyl $\nu_{(C=O)}$ of the pyrazolone ring[40,43-47] has been shifted towards higher wave number in spectra of complexes indicating the linkage between the tellurium atom and carbonyl oxygen atom[,43,45,46]. The band at 1581 cm^{-1} for the azomethine[40,43,45] group of the Schiff base shifted to higher frequency in the IR spectra of aryltellurium complexes due to the bonding of the azomethine nitrogen to tellurium atom. This may be mixed with $\nu_{(C=C)}$ of the $ArTe/Ar_2Te$ moieties. Also, a broad band in Schiff base around 3176 cm^{-1} indicates the presence of phenolic[43,48] OH. This band is slightly shifted to around 3450 cm^{-1} in the Schiff base tellurium complexes, this shows that the hydroxyl group oxygen does not contribute in bonding pattern[48].

The two new bands appear in range 281-293 cm^{-1} and 415-425 cm^{-1} assigned due

to $\nu_{(Te-O)}$[49-52] and $\nu_{(Te-N)}$ mode[53] of vibration.

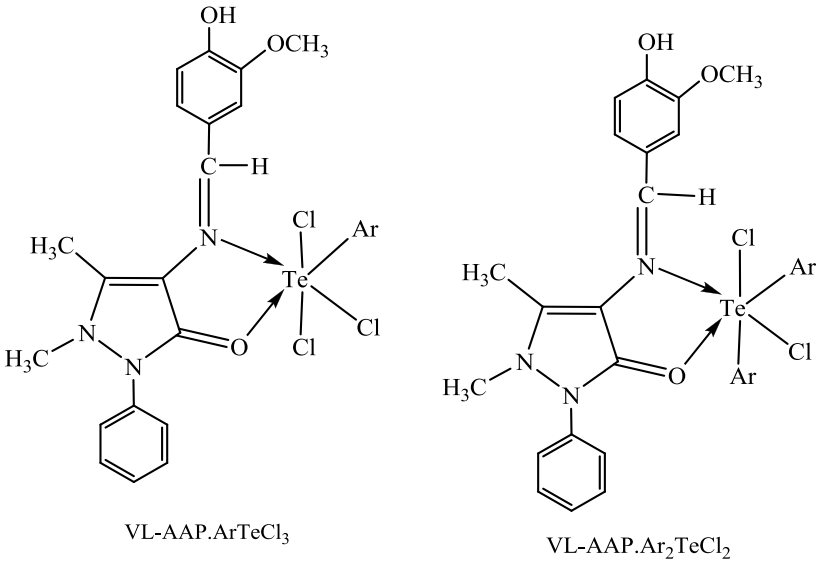
Thus, IR data predict the bidentate nature of the Schiff base(VL-AAP) involving azomethine nitrogen atom and carbonyl oxygen of pyrazolone ring give rise to six membered chelate ring with the tellurium centre having distorted octahedral geometry.

^{1}H NMR Spectra

In order to identify the solution structure of Schiff base (VL-AAP) and its complexes, ^{1}H NMR spectra were recorded in DMSO-d_6. The proton signal for OH group[54] in Schiff base appears[44,45,47] at 9.49 δ ppm as broad singlet and in complexes it resonate at 9.76 δ ppm. This indicates that OH group does not participate in the complexation[45].

The azomethine protons which resonate as a singlet[43,44,46] at 9.47 δ ppm, the coordination of azomethine nitrogen to tellurium in the complexes are clearly demonstrated by a downfield shift of this peak[43]. The signal for *C*-methyl proton (>C-CH_3) attached to pyrazolone ring[43,46] appear at 2.44 δ ppm, while the *N*-methyl proton (>N-CH_3) attachéd to pyrazolone[43,46] appear at 3.45 δ ppm in the spectra of Schiff base and these signal shift to down field in complexes due to the effect of coordination of carbonyl oxygen. The ratios of ligand protons to theArTe/ Ar_2Te protons also confirm the stoichiometry of complexes as 1:1.

Thus, Schiff base(VL-AAP) act as a bidentate –*N*(azomethine), –*O* (carbonyl) chelating ligand in VL-AAP.$ArTeCl_3$ and VL-AAP.Ar_2TeCl_2 complexes giving six coordinate tellurium having *Ψ*-octahedral geometry in these complexes as predicated from IR studies as well. The proposed structures are as below (Figure 1):



VL-AAP.$ArTeCl_3$ VL-AAP.Ar_2TeCl_2

Ar = *p*-methoxyphenyl, *p*-ethoxyphenyl, *p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl

Figure 1. Proposed Structures of Complexes

Biological Activity

The Schiff base (VL-AAP) and newly synthesized aryltellurium(IV) schiff base complexes were evaluated for their antimicrobial activity *in vitro* against Gram +ve bacteria (*S. aureus* ATCC 11632 and *B. cereus* MTCC 7350), Gram -ve bacteria (*E. coli* ATCC 35218, *P. aeruginosa* ATCC 23564, *S. typhi* ATCC 15499 and *P. rettgeri* DRDE) and fungal strains (*A. niger*, *A. fumigates* and *A. flavus*) by tube dilution method[55]. Dilution of test and standard compounds were prepared double strength nutrient broth- I.P (Antibacterial) and Sabouraud Dextrose Broth –I.P (Antifungal)[56]. The samples were incubated at 37±1ºC for 24h (bacteria), 25±1ºC for 7 days (*A. niger*), 30 ±1ºC for 15 days (*A.*

flavus), 35±1ºC for 72hrs (*A. fumigates*) respectively and results were recorded in terms of MIC (The lowest concentration of test substances which inhibited values.

Comparative study of the MIC value for Schiff base (*o*-VAPH) and their tellurium(IV) complexes indicates that the complexes shows higher antimicrobial(bacterial and fungal) activity than Schiff base itself. From the data, the antibacterial activity shows following trend:

VL-AAP.$ArTeCl_3$ > VL-AAP.Ar_2TeCl_2 > VL-AAP Schiff base

And for antifungal activity trend:

VL-AAP.Ar_2TeCl_2 > VL-AAP.$ArTeCl_3$ > VL-AAP Schiff base

Conclusion

Aryltellurium (IV) and diaryltellurium(IV) dichlorides upon reaction with Schiff base(VL-AAP) derived from vanillin and 4-aminoantipyrine yield new 1:1 type complexes of tellurium(IV). The synthesized complexes were characterized by elemental analyses, conductance measurement, IR and ^1H NMR spectral studies. The analytical data suggest that the VL-AAP Schiff base complexes have 1:1 stoichiometry. The Schiff base (VL-AAP) in these complexes acts as a bidentate ligand through oxygen of the pyrazolone ring carbonyl (C=O) and nitrogen atom of azomethine group (CH=N) to give five membered chelate ring with tellurium centre having Ψ-octahedral geometry. The complexes have been observed to possess more antimicrobial activity against bacterial and fungal strains than parent Schiff base.

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