

Synthesis, Characterization, Spectral Studies and antimicrobial Study On Mixed Ligand Complexes of Chloro-arsenic(III) Derived from β -Ketiminates & Piperidine dithiocarbamate Ligand Moity

ABSTRACT

A series of Chloro-arsenic(III) complexes with N, O donor β -ketiminate ligand (L_1) and S, S donor piperidine dithiocarbamate ligand (L_2) have been synthesized by the reactions of $AsCl_3$ with both ligands in equimolar ratio by stirring at room temperature in benzene solution. All these synthesized compounds have been characterized by Elemental Analysis, IR, (1H and ^{13}C) NMR Spectral and ESI-Mass Studies. Both Ligands and their corresponding Chloro-arsenic(III) complexes have been screened for antimicrobial activity against the various bacterial (*E.Coli*, *B.Subtalis* and *P.Aeruginosa*) and fungal (*T.Resei*, *P.Funiculosum* and *Fusarium*) strains and results obtained .

Keyword: - Arsenic-trichloride, Heterocyclic dithiocarbamate, β -Ketiminate, (1H and ^{13}C) NMR Spectral Studies, Antimicrobial Activity.

Introduction

Metal complexes bearing sul-fur donor ligands continues to increase at an unabated pace, because of their resemblance to several important biomolecules, such as amino acids and vitamins ^[1,2]. Dithiocarbamate ligands are organosulfur compounds having remarkable complexing ability and coordination chemistry of these ligand is well documented and established ^[3]. Their complexes are finding newer applications in many areas of chemistry, biology and industry ^[4]. For instance, $(CH_3)_2NCSS^-$ is used for the separation of various metal ions as their

metal chelates ^[5] while its As-Complex / Sn-complex found to possess strong anti-cancer properties ^[6]. Metal complexes with potentially tridentate and tetradentate ligands have evoked much interest in coordination chemistry ^[7].

Schiff base complexes of transition metals have played prominent role in the development of coordination chemistry ^[8]. Simple compounds like AsCl_3 have shown good activity as antimicrobial agents but the study shows the efficiency increases with suitable organic ligands ^[9-12]. Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups, and it is multiplied manifold when the ligands have biological importance ^[13-15].

The number and diversity of nitrogen and sulfur chelating agents used to prepare new coordination and organometallic compounds have increased rapidly during the past few years ^[16-18]. Sulfur compounds and their metal complexes have antimicrobial activity and showed a high dependence on their substituents ^[19,20]. The activity may be due to the presence of multi-coordination centers having the ability to form stable chelates with the essential metal ions which the organisms need in their metabolism. metal complexes of sulfur-nitrogen chelating agents, especially those formed from thiosemicarbazide ^[21] and S-alkyl/benzyl esters of dithiocarbazic acid has been stimulated by their interesting physicochemical properties and potentially useful pharmacological properties ^[22]. Organoarsenic(III) compounds are known to be biologically active and find applications in various fields ^[23]. In addition, the presence of nitrogen and oxygen donor atoms in the complexes makes these compounds effective and stereospecific catalysts for many chemical reaction, biological activity and other transformations of organic and inorganic chemistry^[24].

The focus of our present communication is on the exploration of the studies on the synthetic, structural, and biological aspects of Chloro-arsenic (III)

complexes of some stereochemical as well as biological interest with β -Ketiminates & Piperidine dithiocarbamate ligands.

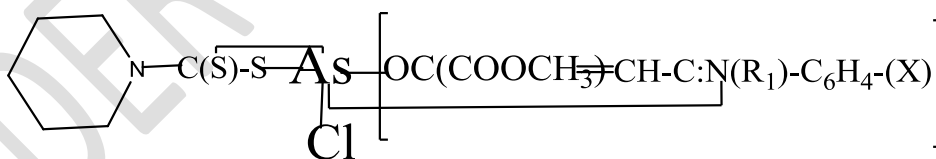
Materials and method

Precautions were taken to exclude moisture through out these studies. The chemicals used were of reagent grade. Piperidine dithiocarbamate (26) and β -ketiminate (27) were synthesized by literature methods. Arsenic and sulphur were estimated by iodometric and gravimetric (28), respectively.

IR Spectra of all these complexes have been recorded as nujol mull using KBr pellets in the range 4000-400 cm^{-1} on FT-IR Spectrophotometer model 8400S SHIMADZU . The ^1H and ^{13}C NMR Spectra have been recorded on JEOL-FTAL 300 MHz Spectrometer in CDCl_3 / DMSO-d_6 Solutions, using TMS as an internal reference.

The complexes were synthesized by the reactions of AsCl_3 , β -ketiminate and piperidine dithiocarbamate in 1:1:1 molar ratio. Complexes were synthesized by two steps since all complexes were synthesized by a similar procedure and synthetic procedure for one of the derivatives is described below in detail.

Synthesis of



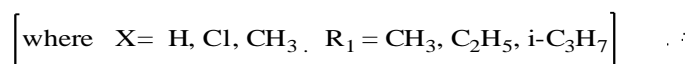
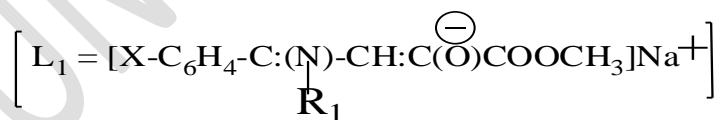
(1). The reaction mixture containing equimolar amount salt of (β ketiminate)(1.17g/2.39m ml) and AsCl_3 (0.99g/2.02m ml) in benzene (50 ml) was stirred for 8 hours at room temperature. NaCl thus formed during the course of the reaction was filtered off and the excess solvent was removed from filterate under reduced pressure to yield the semi solid in quantitative yield. The crude compound was re-crystallized from chloroform and petroleum ether mixture.

(2). An about 30 ml benzene solution of L_1AsCl_2 (1.48g/3.02m ml) was added to benzene suspension (20ml) of sodium salt of piperidine (0.74g/1.51 m ml) and the reaction mixture was stirred for 10 hours. After completion of the reaction, NaCl formed during the course of the reaction, was filtered off. The excess amount of solvent was removed from filterate under reduced pressure to yield the title solid compound in quantitative yield. The crude compound was recrystallized from benzene and n-hexane mixture.

Rest of the compounds has been synthesized by similar method. The synthetic and analytical data are summarized in Table III.

Results and discussion :-

Chloro-arsenic(III) derivatives of β -ketiminate have been synthesized by the reactions of $AsCl_3$ with sodium salts of β -ketiminate (L_1Na) in unimolar ratio with vigorous stirring at room temperature. L_1AsCl_2 viscous liquid derivatives are further reacted with sodium salts of piperidine dithiocarbamate to obtain the desired product in benzene solution at room temperature.



All these derivatives are colored dark brown crystalline solid, soluble in common organic solvents and are re-crystallized by benzene and n-hexane mixture.

IR Spectra :-

IR Spectra of these derivatives have been recorded as KBr-Pellets in the region 4000-400 cm^{-1} . All these Chloro-arsenic(III) (heteroleptic) complexes exhibit a broad band in the region $1540 \pm 10 \text{ cm}^{-1}$ due to $\nu(\text{C}=\text{N})$ imine stretching vibration and their comparison to the corresponding free β -ketiminate ligands show a shifting towards higher frequencies ($\sim 30 \text{ cm}^{-1}$). The disappearances of ν OH absorption band in IR Spectra of all these derivatives as compared to their free corresponding β -ketiminate ligand, which is observed in free ligands at 3070-3120 cm^{-1} . This clearly indicates deprotonation of OH proton as well as formation of *As-O* bond in all these derivatives. The formation of *As-O* bond have been further confirmed by the appearances of new band at 560-590 cm^{-1} . Chloro-arsenic(III) β -ketiminate-complexes exhibit a strong band due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ stretching vibrations at 1740-1630 cm^{-1} and 1300-1070 cm^{-1} respectively due to presence of ester group. The ester group signal shows no appreciable shift in its position in complexes as compared to their corresponding sodium salts of β -ketiminate. A shift has been observed due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ stretching vibrations reveal that the β -ketiminate ligand are coordinated with central arsenic atom in bidentate manner in viscous liquid state of all these derivatives.

Besides these Chloro-arsenic(III)-(heteroleptic) complexes exhibit a strong band at 1445-1470 cm^{-1} due to $\nu(\text{C}=\text{N})$ stretching vibration which are shifted to higher frequencies than the corresponding free sodium salt of piperidine dithiocarbamate moiety. To determine the coordination pattern of dithiocarbamate moiety in these derivatives, the value of $\nu[\nu(\text{CS}_2)_{\text{assy}} - \nu(\text{CS}_2)_{\text{symm}}]$ may be used. The

values of $\nu(\text{CS}_2)_{\text{assy}}$ and $\nu(\text{CS}_2)_{\text{symm}}$ stretching bands for these derivatives appeared at 1130-1150 cm^{-1} and 980-990 cm^{-1} respectively. The ν value [$\nu(\text{CS}_2)_{\text{assy}} - \nu(\text{CS}_2)_{\text{symm}}$] are observed in the region of 140-170 cm^{-1} , which are smaller than the observed $\Delta\nu$ values for bidentate coordinated derivatives and are larger value than the corresponding sodium salt of piperidine dithiocarbamate. The above mentioned data suggest that the piperidine dithiocarbamate moiety is coordinated to arsenic atom in an anisobidentate manner^[26]. A split strong bands in the region 1080-975 cm^{-1} due to $\nu(\text{C}=\text{S})$ stretching vibrations have been observed in all these derivatives as well as corresponding free sodium salt of piperidine dithiocarbamate.

The $\nu(\text{As-S})$ has been observed at 425-445 cm^{-1} and $\nu(\text{As-C})$ has been appeared at 465-475 cm^{-1} in the spectra of all these derivatives.

NMR Spectra

¹H NMR :-

The ¹H NMR Spectra of these Chloro-arsenic(III) derivatives have been recorded in CDCl_3 and DMSO-d_6 and their data are summarized. (Table I)

A comparative study of the ¹H NMR Spectra of these Chloro-arsenic(III)(heteroleptic) derivatives with their corresponding free β -ketiminate ligands shows the disappearance of the OH- signal which is observed at δ 15.00-15.20 in the free β -ketiminate ligand. Methine ($-\text{CH}=\text{}$) proton appeared as a singlet at δ 7.06 - 7.19 and Proton signals due to nitrogen attached CH_3 , C_2H_5 , $-\text{CH}(\text{CH}_3)_2$ group are observed at their appropriate position. A singlet for $-\text{OCH}_3$ proton appeared at δ 3.93 and signals for substituted phenyl protons are found in the region δ 7.18 - 8.28 as multiplet. $-\text{CH}_2-$, $\text{CH}_2\text{-N-CH}_2$ protons in sodium salt of piperidine dithiocarbamate moiety observed at δ 1.68 to 1.76, δ 3.72 to 4.28

respectively, in all these derivatives as well as sodium salt of piperidine dithiocarbamate ligand. No appreciable shift observed in their positions as compared to their corresponding sodium salts of β -ketiminate and dithiocarbamate moiety.

^{13}C NMR Spectra:-

The ^{13}C NMR spectra of all these Chloro-arsenic(III) (heteroleptic) derivatives are interpreted and data are summarized. (Table II)

A comparative study of ^{13}C NMR Spectra of all these Chloro-arsenic(III)(heteroleptic) derivatives with their corresponding β -ketiminates exhibit carbon signals for $\text{C}=\text{C}-\text{OH}$ (C^3) and imine $\text{C}=\text{N}$ (C^2) carbons at δ 172.04-161.98 and δ 190.27 – 186.50 respectively. The position of these carbon signals are deshielded on complexation as compared to their signal position in the free β -ketiminates moiety. This confirms the chelation of arsenic through oxygen atom attached to enolic carbon and nitrogen atom attached to imine carbon. The carbon signals for $(-\text{OCH}_3)$ C^1 observed at δ 53.93-52.27 and phenyl carbons of β -ketiminate moiety are appeared in the region δ 157.91 - 144.83, δ 129.57 - 128.27, δ 140.66 -136.12, δ 128.20-126.19 and may be assigned to $\text{C}_{(\text{i})}\text{C}^6$, $\text{C}_{(\text{o})}\text{C}^7$, $\text{C}_{(\text{m})}\text{C}^8$, $\text{C}_{(\text{p})}\text{C}^9$, respectively.

Besides these ^{13}C NMR Spectra of all these heteroleptic derivatives with their corresponding sodium salt of piperidine dithiocarbamate moiety indicates the remarkable upfield shift of (~ 20 -30 ppm) in the position of CS_2 carbon signal, due to strong chelation and bidentate behaviour of dithiocarbamate moiety. Remaining carbon signals of piperidine dithiocarbamate moiety Chloro-arsenic(III) (heteroleptic) derivatives have been appeared at their expected position as shown in Table II.

ESI-Mass Spectra:-

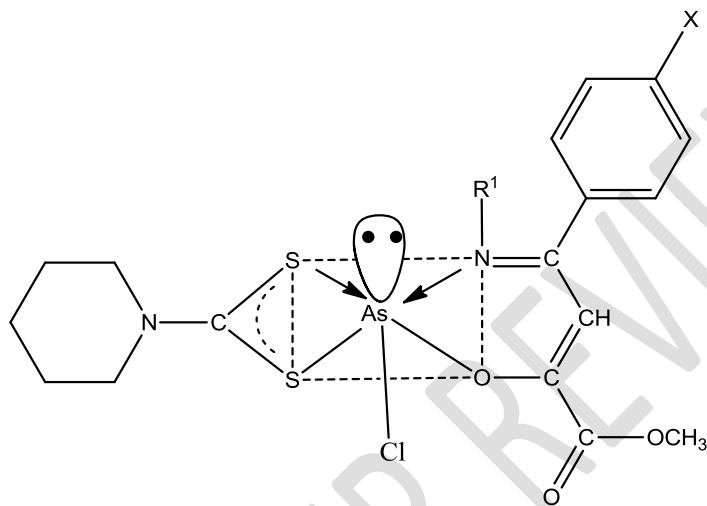
ESI-mass Spectral data of one of the synthesized complexes has been recorded and show revalent mass spectral peaks along with their relative abundance and possible fragmentation patterns are being summarized in Table IV. ESI mass spectrometry is one of the most important methods to determine molecular weight of complexes and to identify the fragments formed during bombardment, which reveal composition and properties of particular moiety of complexes. Two important peaks were observed in ESI mass spectrum; the molecular ion peak, indicating the molecular mass of the complex, which is weak in the case of the complexes investigated, and the base peak, corresponding the fragments { $(\text{Cl})\text{AsSC}_2\text{H}_4^+$ }. These complexes exhibit Monomeric in nature.

Structure elucidation :-

The molecular structure of these Chloro-arsenic(III) (heteroleptic) derivatives in which arsenic atom attached to β -ketiminate and piperidine dithiocarbamate ligand moieties in solid state may be assigned on the basis of earlier reported crystallographic structure of β -ketiminate and heterocyclic dithiocarbamate derivatives^[25]. The downfield shifting has been appered in the position C-OH enolic carbon signal as well as in imine (C=N) carbon signals reveals bidentate behaviour of β -ketiminate moiety in these Chloro-arsenic(III) (heteroleptic) derivatives.

Furthermore ^{13}C NMR Spectral Studies exhibit remarkable upfield shift in the position of CS_2 carbon signal indicating bidentate behaviour of piperidine dithiocarbamate or strong chelation in these derivatives. The above mentioned spectroscopic evidences exhibit that the dithiocarbamate moiety and β -ketiminate other monofunctional moiety both are coordinated with antimony atom in bidentate

manner. Therefore the following structures in which arsenic atom acquires distorted octahedral geometry having stereo-chemical active lone pair of electron may be assigned for Chloro-arsenic(III) (heteroleptic) derivatives having β -ketiminates and piperidine dithiocarbamate.



[Where X = H, Cl, CH₃, C₂H₅, C₃H₇]

Biological activity:-

Heteroleptic derivatives of Chloroarsenic (III) and corresponding free ligands were screened against *T.resei*, *P.Funiculosum* and *fusarium*(fungi), *B.subtalis*, *P.aeruginosa* and *E.coli* (bacteria) to examine their inhibition zone towards the tested microorganisms. The results indicate that the metal derivatives were more inhibitory than corresponding ligands. It shows higher activity due to presence of Chlorine and then chelation agent itself. The enhanced activity of metal derivatives may be ascribed to the increased lipophilic nature of these derivatives arising due to chelation. The observed toxicity with bacteria and fungi can be explained on the basis of the Tweedy's chelation theory and overtone's concept⁽²⁹⁾. The results indicate that 1-6 > L₁- L₁₀ the data are summarized in Table V and VI.

Conclusion

The present research is on the exploration of the studies on the synthetic, structural, and biological aspects of Chloro-arsenic (III) complexes of some stereochemical as well as biological interest with β -Ketiminates & Piperidine dithiocarbamate ligands. ^{13}C NMR Spectral Studies exhibit remarkable upfield shift in the position of CS_2 carbon signal indicating bidentate behaviour of piperidine dithiocarbamate or strong chelation in these derivatives.

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TableI. ¹H NMR Spectral data (δ) of Chloro-Arsenic(III) (heteroleptic) derivatives.



| Compounds | N-(R ₁) | CH ₃ -Ph | -OCH ₃ | -CH | -C ₆ H ₄ -X |  |  |
|--|---------------------|---------------------|-------------------|------|-----------------------------------|--|--|
| Compound 1 R ₁ = CH ₃ ; X = H | 2.65 | - | 3.93 | 7.18 | 7.36-7.82 | 1.69 | 4.03 |
| Compound 2 R ₁ = C ₂ H ₅ ; X = H | 3.96, 1.71 | - | 3.89 | 7.32 | 7.30-7.44 | 1.68 | 3.91 |
| Compound 3 R ₁ = C ₃ H ₇ ; X = H | 1.42, 3.81, 4.01 | -- | 3.81 | 7.18 | 7.18-7.50 | 1.71 | 3.90 |
| Compound 4 R ₁ = CH ₃ ; X = -Cl | 2.41 | - | 3.69 | 7.34 | 7.32-7.80 | 1.60 | 3.64 |
| Compound 5 R ₁ = C ₂ H ₅ ; X = -Cl | 3.76, 1.72 | - | 3.77 | 7.30 | 7.52-7.84 | 1.72 | 3.79 |
| Compound 6 R ₁ = C ₃ H ₇ ; X = -Cl | 1.44, 3.82, 3.86 | - | 3.83 | 7.22 | 7.42-7.90 | 1.65 | 3.68 |
| Compound 7 R ₁ = CH ₃ ; X = CH ₃ | 2.49 | 2.41 | 3.97 | 7.15 | 7.33-7.84 | 1.68 | 3.84 |
| Compound 8 R ₁ = C ₂ H ₅ ; X = CH ₃ | 1.82, 3.81 | 2.40 | 3.90 | 7.27 | 7.28-7.91 | 1.72 | 3.78 |
| Compound 9 R ₁ = C ₃ H ₇ ; X = CH ₃ | 1.58, 3.81, 4.01 | 2.39 | 3.96 | 7.17 | 7.37-7.93 | 1.74 | 3.73 |

Table II. ^{13}C NMR Spectral data (δ) of Chloro-Arsenic(III) (heteroleptic) derivatives.

| Compounds | C ₂ | C ₅ | C ₃ | C ₆ | C ₈ | C ₇ | C ₉ | C ₄ | C ₁ | Ph-CH ₃ | As-Ph | C _a | C _b | C _c | C _d |
|---|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|--------------------|----------------------------------|----------------|----------------|----------------|----------------|
| Compound 1 R ₁ =CH ₃ ; X = H | 186.45 | 169.45 | 162.70 | 148.55 | 139.44 | 128.27 | 127.34 | 92.77 | 53.04 | - | 138.34, 136.60 130.70, 129.27 | 23.85 | 25.79 | 51.94 | 196.91 |
| Compound 2 R ₁ =C ₂ H ₅ ; X = H | 189.48 | 169.65 | 162.30 | 157.91 | 137.91 | 128.88 | 126.19 | 97.74 | 53.89 | - | 137.11, 136.54 130.98, 129.88 | 21.15 | 25.59 | 55.12 | 197.25 |
| Compound 3 R ₁ =C ₃ H ₈ ; X = H | 189.53 | 169.28 | 162.47 | 152.01 | 140.36 | 128.32 | 127.04 | 97.94 | 53.44 | - | 138.16, 135.74 129.87, 127.86 | 23.33 | 26.61 | 53.34 | 193.28 |
| Compound 4 R ₁ =CH ₃ ; X = -Cl | 187.94 | 179.04 | 172.04 | 150.02 | 136.88 | 128.83 | 127.98 | 94.76 | 52.96 | - | 136.19, 134.83 128.76, 127.89 | 23.92 | 25.77 | 52.96 | 198.29 |
| Compound 5 R ₁ =C ₂ H ₅ ; X = -Cl | 186.50 | 170.12 | 167.13 | 149.11 | 140.66 | 129.19 | 127.82 | 96.13 | 53.93 | - | 136.85, 129.73 127.87, 126.92 | 23.06 | 27.11 | 51.10 | 195.83 |
| Compound 6 R ₁ =C ₃ H ₈ ; X = -Cl | 187.07 | 173.27 | 164.27 | 153.91 | 136.12 | 128.68 | 126.27 | 97.79 | 52.27 | - | 137.77, 136.87 131.11, 127.67 | 26.63 | 28.12 | 60.58 | 198.38 |
| Compound 7 R ₁ =CH ₃ ; X =CH ₃ | 190.20 | 168.26 | 163.70 | 146.59 | 133.72 | 129.57 | 127.05 | 97.89 | 53.05 | 29.23 | 139.75, 137.55 129.85, 128.79 | 23.02 | 29.36 | 53.89 | 197.12 |
| Compound 8 R ₁ =C ₂ H ₅ ; X=CH ₃ | 190.27 | 172.27 | 170.09 | 152.11 | 139.72 | 128.72 | 128.20 | 97.36 | 53.56 | 31.13 | 139.70, 136.55 130.47, 127.50 | 21.89 | 28.70 | 51.72 | 198.45 |
| Compound 9 R ₁ =C ₃ H ₈ ; X=CH ₃ | 189.07 | 168.10 | 161.98 | 144.43 | 138.17 | 128.04 | 126.71 | 96.72 | 52.44 | 28.97 | 138.48, 132.26 131.99, 129.50 | 22.52 | 27.12 | 51.23 | 194.32 |

Table III. Synthetic and Analytical data of Chloro-Arsenic(III) (heteroleptic) derivatives.

| Complex | Reactant (gm) /m ml | | | | % Yields empirical formula | NaCl (g) Found (Calc) | Analysis | | Molecular weight Found (Calc) |
|--|---|-------------|---|-------------|--|--------------------------------|------------------|------------------|--|
| | Sodium Salt of Ligands L ₁ H L ₂ Na | | AsCl ₃ AsCl ₃ L ₁ AsCl ₂ | | | | As% | S % | |
| | | | | | | Found (Calc) | Found (Calc) | Found (Calc) | |
| Compound 1 R ₁ = CH ₃ ; X = H | 1.17 / 2.39 | 0.74 / 1.51 | 0.99 / 2.02 | 1.48 / 3.02 | 76 C ₁₈ H ₂₂ AsO ₃ S ₂ N ₂ Cl | 0.70 (0.65) | 15.90 (15.30) | 13.70 (13.09) | 488.80 (488.20) |
| Compound 2 R ₁ = C ₂ H ₅ ; X = H | 1.20 / 2.38 | 0.72 / 1.43 | 0.95 / 1.88 | 1.50 / 2.98 | 72 C ₁₉ H ₂₄ AsO ₃ S ₂ N ₂ Cl | 0.75 (0.63) | 15.15 (14.90) | 12.95 (12.70) | 502.90 (502.70) |
| Compound 3 R ₁ = C ₃ H ₇ ; X = H | 1.28 / 2.48 | 0.70 / 1.35 | 0.92 / 1.78 | 1.51 / 2.90 | 75 C ₂₀ H ₂₆ AsO ₃ S ₂ N ₂ Cl | 0.75 (0.61) | 15.10 (14.50) | 12.90 (12.40) | 516.10 (516.20) |
| Compound 4 R ₁ = CH ₃ ; X = -Cl | 1.21 / 2.31 | 0.70 / 1.33 | 0.91 / 1.73 | 1.52 / 2.90 | 74 C ₁₈ H ₂₁ AsO ₃ N ₂ S ₂ Cl ₂ | 0.71 (0.61) | 14.50 (14.30) | 12.50 (12.30) | 523.70 (523.30) |
| Compound 5 R ₁ = C ₂ H ₅ ; X = -Cl | 1.23 / 2.28 | 0.68 / 1.26 | 0.89 / 1.65 | 1.50 / 2.79 | 79 C ₁₉ H ₂₃ AsO ₃ N ₂ S ₂ Cl ₂ | 0.70 (0.60) | 14.50 (13.98) | 12.20 (11.90) | 537.40 (537.80) |
| Compound 6 R ₁ = C ₃ H ₇ ; X = -Cl | 1.26 / 2.28 | 0.67 / 1.21 | 0.87 / 1.57 | 1.48 / 2.68 | 71 C ₂₀ H ₂₅ AsO ₃ S ₂ N ₂ Cl ₂ | 0.67 (0.61) | 14.05 (13.58) | 12.04 (11.75) | 551.50 (551.45) |
| Compound 7 R ₁ = CH ₃ ; X = CH ₃ | 1.20 / 2.38 | 0.72 / 1.43 | 0.95 / 1.88 | 1.50 / 2.98 | 68 C ₁₉ H ₂₄ AsO ₃ S ₂ N ₂ Cl | 0.72 (0.62) | 15.10 (14.89) | 13.02 (12.70) | 503.10 (503.10) |
| Compound 8 R ₁ = C ₂ H ₅ ; X = CH ₃ | 1.28 / 2.46 | 0.70 / 1.33 | 0.92 / 1.87 | 1.51 / 2.96 | 71 C ₂₀ H ₂₆ AsO ₃ S ₂ N ₂ Cl | 0.70 (0.62) | 14.90 (14.50) | 12.94 (12.72) | 515.60 (515.50) |
| Compound 9 R ₁ = C ₃ H ₇ ; X = CH ₃ | 1.27 / 2.39 | 0.71 / 1.33 | 0.93 / 1.75 | 1.49 / 2.80 | 69 C ₂₁ H ₂₈ AsO ₃ S ₂ N ₂ Cl | 0.69 (0.60) | 14.60 (14.16) | 12.60 (12.07) | 530.20 (530.10) |

Table IV. ESI-Mass Fragmentation Mode of Compounds 1.

| S.No. | Assignment | Mass No. | Relative abundance % |
|-------|--|----------|----------------------|
| 1. | (Cl)AsO ₃ S ₂ N ₂ C ₁₈ H ₂₂ ^{+·} | 488.80 | 12.01/15.50 |
| 2. | (Cl)AsSO ₃ C ₁₈ H ₂₂ ^{+·} | 428.10 | 21.32/ 15.30 |
| 3. | (Cl)AsSC ₁₀ H ₁₄ ^{+·} | 355.20 | 14.15/ 21.30 |
| 4. | (Cl)AsSC ₇ H ₄ ^{+·} | 274.20 | 100 |
| 5. | (Cl)AsSC ₂ H ₂ ^{+·} | 168.60 | 9.30/15.20 |
| 6. | As-S ^{+·} | 108.74 | 27.10/35.20 |

Table V. Inhibiton Zone of Sodium salts of β -Ketimate (L₁₋₉)and Pipridine dithiocarbamate (L₁₀) against Bacteria and Fungi.

| Microorganisms | L₁ | L₂ | L₃ | L₄ | L₅ | L₆ | L₇ | L₈ | L₉ | L₁₀ |
|-------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|-----------------------|
| <i>T.Resei (fungi)</i> | 15 | 03 | 19 | 20 | 16 | 12 | 14 | 17 | 12 | 21 |
| <i>P.Funiculosum(fungi)</i> | 20 | 02 | 22 | 08 | 14 | 19 | 17 | 06 | 16 | 16 |
| <i>Fusarium (fungi)</i> | 22 | 21 | 08 | 09 | 12 | 07 | 11 | 20 | 13 | 19 |
| <i>B.Subtalis (bacteria)</i> | 17 | 03 | 19 | 20 | 07 | 15 | 00 | 13 | 15 | 14 |
| <i>P.Aeruginosa(bacteria)</i> | 05 | 12 | 15 | 08 | 14 | 12 | 14 | 07 | 09 | 19 |
| <i>E.Coli (bacteria)</i> | 15 | 04 | 20 | 12 | 17 | 00 | 11 | 15 | 17 | 15 |

Table VI. Inhibition Zone of Chloro-Arsenic(III) (Heteroleptic) Derivatives against Bacteria and Fungi.

| Microorganisms | Compd 1 | Compd 2 | Compd 3 | Compd 4 | Compd 5 | Compd 6 | Compd 7 | Compd 8 | Compd 9 |
|--------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| <i>T. Resei (fungi)</i> | 17 | 06 | 19 | 17 | 18 | 15 | 09 | 12 | 10 |
| <i>P.Funiculosum(fungi)</i> | 21 | 08 | 06 | 22 | 15 | 09 | 17 | 15 | 12 |
| <i>Fusarium (fungi)</i> | 14 | 18 | 05 | 18 | 07 | 14 | 14 | 09 | 14 |
| <i>B. Subtalis (bacteria)</i> | 18 | 10 | 06 | 11 | 17 | 10 | 09 | 14 | 09 |
| <i>P.Aeruginosa (bacteria)</i> | 05 | 07 | 18 | 08 | 20 | 06 | 16 | 20 | 18 |
| <i>E.Coli (bacteria)</i> | 09 | 12 | 10 | 03 | 09 | 15 | 10 | 13 | 10 |