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

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Authors' contributions

This work was carried out in collaboration among all authors. Author DKS designed the study, performed the chemical analysis, wrote the protocol and wrote the first draft of the manuscript and also managed literature survey. Author JS guided me as my supervisor and author RS guided me as well as contributed in evaluating biological activities in this research. All authors read and approved the final manuscript.

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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.

Keywords: Arsenic-trichloride; Heterocyclic dithiocarbamate; β-Ketiminate; (^1H and ^{13}C) NMR spectral studies; antimicrobial activity.

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1. 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, $(CH3)2NCSS^-$ 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.

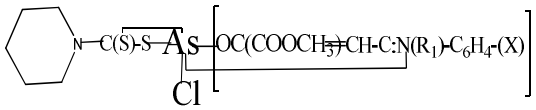
2. MATERIALS AND METHODS

Precautions were taken to exclude moisture throughout these studies. The chemicals used were of reagent grade. Piperidine dithiocarbamate [25] and β-ketiminate [26] were synthesized by literature methods. Arsenic and sulphur were estimated by iodometric and gravimetric [27], 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 13C NMR Spectra have been recorded on JEOL-FTAL 300 MHz Spectrometer in CDCl3 / DMSO-d6 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) (1.17 g/2.39 m ml) and $AsCl_3$ (0.99 g/2.02 m ml) in benzene (50 ml) was stirred for 8 hours at room temparature. NaCl thus formed during the course of the reaction was filtered off and the excess solvent was removed from filterate under redued pressure to yield the semi solid in quantitave yield. The crude compound was re-crystallized from chloroform and petroleum ether mixture.

2. An about 30 ml benzene solution of L_1AsCl_2 (1.48 g/3.02 m ml) was added to benzene suspension (20 ml) of sodium salt of piperidine (0.74 g/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 redued pressure to yield the title solid compound in quantitave yield. The crude compound was recrystallized from benzene and n-haxene mixture.

Rest of the compounds has been synthesized by similar method. The synthetic and analytical data are summarized in Table 3.

3. 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 viscuss liquid derivatives are further reacted with sodium salts of piperidine dithiocarbamate to obtain the desired product in benzene solution at room temperature.

$$AsCl_3 + L_1Na \longrightarrow L_1AsCl_2 + NaCl\downarrow$$

$$L_1AsCl_2 + L_2Na \longrightarrow L_1AsL_2Cl + NaCl\downarrow$$

$$\left[L_1 = [X\text{-}C_6H_4\text{-}C(R_1):N\text{-}CH:C(\ominus)O)COOCH_3]Na^+\right]$$

$$\left[\text{where } X = H, Cl, CH_3,\ R_1 = CH_3, C_2H_5, i\text{-}C_3H_7\right]$$

$$\left[L_2 = \overline{CH_2CH_2XCH_2CH_2N}CS_2Na\right]$$

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

3.1 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 ± 10 cm^{-1} due to *ν(C=N)* imine stretching vibration and their comparison to the corresponding free β-ketiminate ligands show a shifting towards higher frequencies (~30 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 *ν(C=O)* and *ν(C-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 *ν(C=N)* and *ν(C-O)* stretching vibrations reveal that the β-ketiminate ligand are coordinated with central arsenic atom in bidentate manner in viscuss liquid state of all these derivatives.

Besides these Chloro-arsenic(III)-(heteroleptic) complexes exhibit a strong band at 1445-1470 cm^{-1} due to *ν(C ---- 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 *ν*[$\nu(CS_2)_{assy}$ - $\nu(CS_2)_{symm}$] may be used. The values of $\nu(CS_2)_{assy}$ and $\nu(CS_2)_{symm}$ stretching bands for these derivatives appeared at 1130-1150 cm^{-1} and 980-990 cm^{-1} respectively. The *ν* value [$\nu(CS_2)_{assy}$ - $\nu(CS_2)_{symm}$] 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 [25]. A split strong bands in the region 1080-975 cm^{-1} due to *ν(C=S)* stretching vibrations have been observed in all these derivatives as well as corresponding free sodium salt of piperidine dithiocarbamate.

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

3.2 NMR Spectra

^{1}H NMR: The ^{1}H NMR Spectra of these Chloro-arsenic(III) derivatives have been recorded in

$CDCl_3$ and DMSO-d_6 and their data are summarized (Table 1).

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 (–CH=) proton appeared as a singlet at δ 7.06 - 7.19 and Proton signals due to nitrogen attached CH_3, C_2H_5 , -$CH(CH_3)_2$ group are observed at their appropriate position. A singlet for $–OCH_3$ proton appeared at δ 3.93 and signals for substituted phenyl protons are found in the region δ 7.18 - 8.28 as multiplet. -CH_2-, CH_2-N-CH_2 protons in sodium salt of piperidine dithicarbamate moiety observed at δ1.68 to 1.76, δ 3.72 to 4.28 respectively, in all these derivatives as well as sodium salt of piperidine dithiocarbamate ligand. No appereciable shift observed in their positions as compared to their corresponding sodium salts of β-ketiminate and dithiocarbamate moiety.

3.3 ^{13}C NMR Spectra

The ^{13}C NMR spectra of all these Chloro-arsenic(III) (heteroleptic) derivatives are interpreted and data are summarized (Table 2).

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 $\overset{---}{C}$-OH (C^3) and imine C=N (C^2) carbons at and δ 172.04-161.98 and δ 190.27 – 186.50 respectively. The position of these carbon signals are deshieled 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 (-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 $C_{(i)}C^6$, $C_{(O)}C^7$, $C_{(m)}C^8$, $C_{(P)}C^9$, respectively.

Besides these ^{13}C NMR Spectra of all these heteroleptic derivatives with their corresponding sodium salt of piperidine dithicabamate 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 dithicarbamate moiety. Remaining carbon signals of piperidine dithiocarbamate moiety Chloro-arsenic (III) (heteroleptic) derivatives have been appeared at their expected position as shown in Table 2.

3.4 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 4. 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{ $(Cl)AsSC_2H_4^+$ }. These complexes exhibit Monomeric in nature.

3.5 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 [28]. 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 aquires 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.

Table 1. ^{1}H NMR Spectral data (δ) of Chloro-Arsenic(III) (heteroleptic) derivatives

Compounds	**N-(R_1)**	CH_3-Ph	-OCH_3	-CH	-C_6H_4-X	CH_2 CH_2 CH_2	CH_2
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_2H_5; X = H	3.96, 1.71	-	3.89	7.32	7.30-7.44	1.68	3.91
Compound 3 R_1 = C_3H_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_2H_5 ; X = -Cl	3.76, 1.72	-	3.77	7.30	7.52-7.84	1.72	3.79
Compound 6 R_1 = C_3H_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_2H_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_3H_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 2. ^{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_2H_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_3H_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_2H_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_3H_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_2H_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_3H_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 3. 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		$AsCl_3$				As% found (Calc)	S % found (Calc)	
	L_1H	L_2Na	$AsCl_3$	L_1AsCl_2					
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 $C_{18}H_{22}AsO_3S_2N_2Cl$	0.70 (0.65)	15.90(15.30)	13.70 (13.09)	488.80 (488.20)
Compound 2 $R_1 = C_2H_5$; X = H	1.20/ 2.38	0.72 / 1.43	0.95 /1.88	1.50 / 2.98	72 $C_{19}H_{24}AsO_3S_2N_2Cl$	0.75 (0.63)	15.15 (14.90)	12.95 (12.70)	502.90 (502.70)
Compound 3 $R_1 = C_3H_7$; X = H	1.28/ 2.48	0.70 /1.35	0.92 / 1.78	1.51 / 2.90	75 $C_{20}H_{26}AsO_3S_2N_2Cl$	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 $C_{18}H_{21}AsO_3N_2S_2Cl_2$	0.71 (0.61)	14.50 (14.30)	12.50 (12.30)	523.70 (523.30)
Compound 5 $R_1 = C_2H_5$; X = -Cl	1.23 / 2.28	0.68 / 1.26	0.89/1.65	1.50/ 2.79	79 $C_{19}H_{23}AsO_3N_2S_2Cl_2$	0.70 (0.60)	14.50 (13.98)	12.20 (11.90)	537.40 (537.80)
Compound 6 $R_1 = C_3H_7$; X = -Cl	1.26/ 2.28	0.67/1.21	0.87 / 1.57	1.48/ 2.68	71 $C_{20}H_{25}AsO_3S_2N_2Cl_2$	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 $C_{19}H_{24}AsO_3S_2N_2Cl$	0.72 (0.62)	15.10 (14.89)	13.02 (12.70)	503.10 (503.10)
Compound 8 $R_1 = C_2H_5$; X = CH_3	1.28 / 2.46	0.70/ 1.33	0.92/ 1.87	1.51 / 2.96	71 $C_{20}H_{26}AsO_3S_2N_2Cl$	0.70 (0.62)	14.90 (14.50)	12.94 (12.72)	515.60(515.50)
Compound 9 $R_1 = C_3H_7$; X = CH_3	1.27 / 2.39	0.71 /1.33	0.93 / 1.75	1.49 / 2.80	69 $C_{21}H_{28}AsO_3S_2N_2Cl$	0.69 (0.60)	14.60 14.16)	12.60. (12.07)	530.20 (530.10)

Table 4. ESI-Mass fragmentation mode of compounds 1

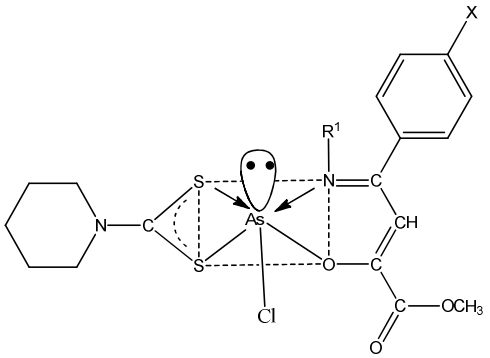
S.No.	Assignment	Mass No.	Relative abundance %
1.	$(Cl)AsO_3S_2N_2C_{18}H_{22}^{+}$	488.80	12.01/15.50
2.	$(Cl)AsSO_3C_{18}H_{22}^{+}$	428.10	21.32/ 15.30
3.	$(Cl)AsSC_{10}H_{14}^{+}$	355.20	14.15/ 21.30
4.	$(Cl)AsSC_7H_4^{+}$	274.20	100
5.	$(Cl)AsSC_2H_2^{+}$	168.60	9.30/15.20
6.	$As\text{-}S^{+}$	108.74	27.10/35.20

Table 5. Inhibiton zone of sodium salts of β-Ketiminate (L_{1-9})and pipridine dithiocarbamate (L_{10}) against Bacteria and Fungi

Microorganisms	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9	L_{10}
T. Resei (fungi)	15	03	19	20	16	12	14	17	12	21
P. Funiculosum(fungi)	20	02	22	08	14	19	17	06	16	16
Fusarium (fungi)	22	21	08	09	12	07	11	20	13	19
B. Subtalis (bacteria)	17	03	19	20	07	15	00	13	15	14
P. Aeruginosa(bacteria)	05	12	15	08	14	12	14	07	09	19
E.Coli (bacteria)	15	04	20	12	17	00	11	15	17	15

Table 6. 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
T. Resei (fungi)	17	06	19	17	18	15	09	12	10
P.Funiculosum(fungi)	21	08	06	22	15	09	17	15	12
Fusarium (fungi)	14	18	05	18	07	14	14	09	14
B. Subtalis (bacteria)	18	10	06	11	17	10	09	14	09
P. Aeruginosa (bacteria)	05	07	18	08	20	06	16	20	18
E. Coli (bacteria)	09	12	10	03	09	15	10	13	10



[Where X = H, Cl, CH_3 : CH_3, C_2H_5, C_3H_7]

3.6 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 liphophilic nature of these derivatives arising due to chelation. The observed toxicity with becteria 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 > L_1- L_{10} the data are summarized in Tables 5 and 6.

4. 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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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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