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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDY OF CHLORO-BISMUTH(III) DERIVATIVES SUPPORTED BY BOTH β-KETIMINATE AND DITHIOCARBAMATE LIGANDS

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ABSTRACT

Nine new mixed N, O and S donor ligand derivatives of Chloro-bismuth(III)-Complexes have been synthesized by the reaction of $BiCl_3$ with both β-Ketiminate and Piperidine dithiocarbamate ligands in equimolar ratio by stirring at room temperature in benzene solution. All these synthesized compounds have been characterized on the basis of elemental analysis, molecular weight measurement, IR, (^{1}H and ^{13}C) NMR and ESI-mass spectral studies. Both the free Ligands and their synthesized complexes were screened for their antimicrobial activity against the various bacterial and fungal strains and exhibited promising results.

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

1. INTRODUCTION

Interest in the rich coordination chemistry of organo-bismuth (III) complexes have attracting increasing attention due to their application in heterogeneous chemical catalysis [1], catalysts for organic synthesis [2], superconducting materials [3], biological activity [4] and as precursors in advanced material science [5]. The sustained interest in bismuth(III) compounds is associated with S donor ligands tendency to show great remarkable structural diversity [6, 7] along with their extensive application as NO trapping agent [8], lubricant [9] and antioxidantents / oil additives [10].

Important property of such derivatives of bismuth(III) would be attached via a sulphur donor atoms e.g N or S and exhibits highly variable coordination and often an irregular coordination geometry [11-13]. However, main-group metal complexes with dithiocarbamate have been rarely studied and few reports have appeared on the bismuth (III) complexes with dithiocarbamate ligands [14-16]. Some bismuth compounds show potential as radio-therapeutic agents use in lymphoma and other tumors [17].

Recently, the chemistry of hypervalent compounds bearing haviour pnictogens (in particular Sb, Bi) has attracted interest as well as the majority of these complexes contain C,N and N,O ligands have beeen applied to stabilize organo-bismuth molecular complexes, cations, or compounds containing metal-metal bonds [18, 19].

In our present communication, we report synthesis, spectral characterization and antimicrobial activity of some new heterocyclic N, S and O-cheated Chloro-bismuth(III) derivatives.

2. EXPERIMENTAL

Precautions were taken to exclude moisture throughout these studies. The chemicals used were of reagent grade. Piperidine dithiocarbamate [20], β-ketiminate [21] was synthesized by literature method. Antimony and sulfur were determined by iodometrically and gravimetric methods [22], 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 ^{1}H 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 $BiCl_3$, 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.

2.1. Synthetic protocol

2.1.1. The reaction mixture containing equimolar amount salt of L_1H (0.87g/1.39 m/ml) and $BiCl_3$ (1.26g/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 filtrate under reduced pressure to yield the viscous liquid in quantitative yield. The crude compound was recrystallized from chloroform and petroleum ether mixture.

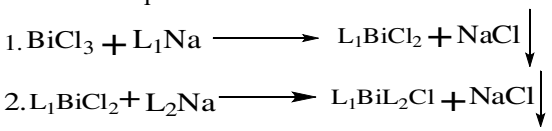
2.1.2. About 30 ml benzene solution of L_1BiCl_2 (1.17g/1.87m/ml) was added to benzene suspension (20ml) of sodium salt of piperidine (0.58g /0.93m/ml) and the reaction mixture was stirred for 10 hours. After completion of the reaction, NaCl formed during the course of the reaction, was filtered off. The excess amount of solvent was removed from filtrate under reduced pressure to yield the title solid compound in quantitative yield. The crude compound was recrystallized from benzene and n-hexane mixture.

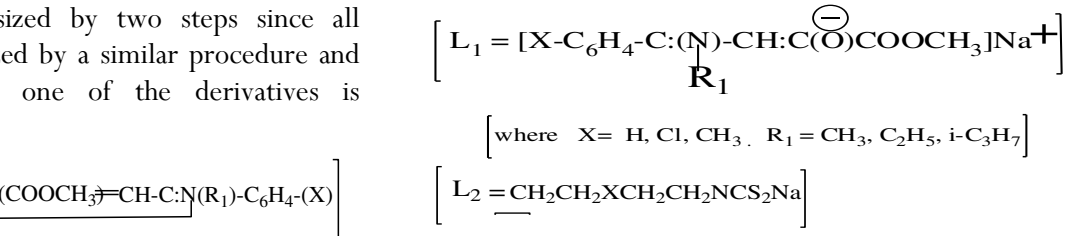
Rest of the compounds had been synthesized by similar method. The synthetic and analytical data are summarized in Table 3.

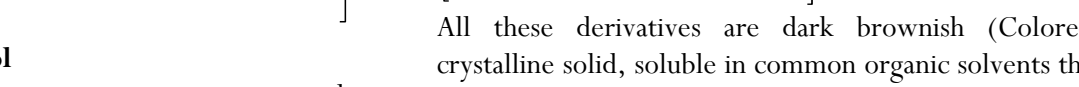
3. RESULTS AND DISCUSSION

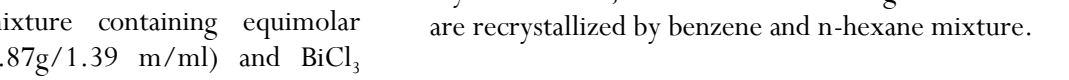
Chloro-bismuth(III) derivatives of β-ketiminate have been synthesized by reaction of $BiCl_3$ with sodium salts of β- ketiminate (L_1Na) in anhydrous benzene solution in 1:1 molar ratio with vigorous stirring at room temperature .

L_1BiCl_2 viscous liquid derivatives are further reacted with sodium salts of piperidine dithiocarbamate to produce the desire product in benzene solution with vigorous stirring at room temperature.









All these derivatives are dark brownish (Colored) crystalline solid, soluble in common organic solvents that are recrystallized by benzene and n-hexane mixture.

3.1. IR Spectra

IR Spectra of these derivatives have been recorded as KBr-Pallets in the region 4000-400 cm^{-1}.All these Chloro-bismuth(III) (heteroleptic) complexes exhibit a broad band in the region 1540 ± 20 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 (~25cm^{-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 3080-3160 cm^{-1}. This clearly indicates deprotonation of OH proton as well as formation of *Bi-O* bond in all these derivatives. The formation of *Bi-O* bond have been further confirmed by the appearances of new band at 550-570 cm^{-1}. Chloro-bismuth(III) β-ketiminate exhibit a strong band due to *ν(C=O)* and *ν(C-O)* stretching vibrations at 1755-1655 cm^{-1} and 1300-1080 cm^{-1} respectively due to 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 bismuth atom in bidentate manner in viscus liquid state of all these derivatives.

Besides these Chloro-bismuth(III) (heteroleptic) complexes exhibit a strong band at 1445-1455 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 $\nu[\nu(CS_2)_{assy} - \nu(CS_2)_{symm}]$ may be used. The values of $\nu(CS_2)_{assy}$ and $\nu(CS_2)_{symm}$ stretching bands for these derivatives appeared at 1135-1145 cm^{-1} and 975-985 cm,$^{-1}$ respectively. The *ν* value $[\nu(CS_2)_{assy} - \nu(CS_2)_{symm}]$ are observed in the region of 120-145 cm^{-1}, which are smaller than the observed Δ*ν*

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 bismuth atom in an anisobidentate manner. A split strong bands in the region 1050-970 cm^{-1} due to *v(C=S)* stretching vibrations have been observed in all these derivatives as well as corresponding free sodium salt of Piperidine dithiocarbamate.

The *v(Bi-S)* has been observed at 415 - 430 cm^{-1} and *v(Bi-C)* has been appeared at 450 - 470 cm^{-1} in the spectra of all these derivatives.

3.2. ^{1}H NMR Spectra

The ^{1}H NMR Spectra Chloro-bismuth(III)-(heteroleptic) derivatives have been recorded in $CDCl_3$ and DMSO-d_6 and their data summarized (Table 1).

A comparison of the ^{1}H NMR Spectra of these Chloro-bismuth -(III) (heteroleptic) derivatives with the corresponding their free β-ketiminate ligands shows the disappearance of the OH- signal which is observed at δ 15.00-15.35 in the free ligands. methine (–CH=) proton also as a singlet at δ 7.29 - 7.61. Signals for phenyl protons attached antimony atom are found in the region δ 7.84 - 8.65 are observed as multiplet. (-CH_2-), (CH_2-N-CH_2) proton in sodium salt of dithicarbamate observed at δ1.68 to δ1.91, δ3.79 to 4.91 respectively, in all these derivatives as well as sodium salts of dithiocarbamate ligand. Signals for CH_3, CH_2-CH_3, CH_3-CH(NH)-CH_3, δ 2.61, δ 3.86, δ 1.71, δ 1.83, δ 4.56, δ 3.72 respectively, in β-ketiminate ligand. No appereciable shift observed in their positions as compaired to these derivatives to their corresponding both sodium salts of β-ketiminate and dithiocarbamate ligand.

Table 1: ^{1}H NMR Spectral Data (δ) of Chloro-Bismuth(III) (Heteroleptic) derivatives

Compound	N-(R_1)	CH_3-Ph	-OCH_3	-CH	-C_6H_4-X	CH_2 CH_2 CH_2	C–N CH_2 CH_2
Compound 1 R_1 = CH_3 ; X = H	2.58	-	4.50	7.56	7.95 - 7.99	1.78	4.52
Compound 2 R_1 = C_2H_5; X = H	3.91, 1.83	-	3.86	7.45	7.94 - 8.15	1.83	4.25
Compound 3 R_1 = C_3H_8 ; X = H	1.71, 3.69, 4.02	--	3.95	7.29	7.97 – 8.09	1.71	4.91
Compound 4 R_1 = CH_3 ; X = -Cl	2.61	-	3.83	7.45	7.98 - 8.07	1.89	4.84
Compound 5 R_1 = C_2H_5 ; X = -Cl	3.17, 1.98	-	3.49	7.40	7.84 -7.93	1.84	3.98
Compound 6 R_1 = C_3H_8 ; X = -Cl	2.60, 3.72, 4.56	-	3.90	7.54	7.98 - 8.03	1.71	3.93
Compound 7 R_1 = CH_3 ; X = CH_3	2.63	2.58	4.03	7.38	7.96 – 8.12	1.82	3.79
Compound 8 R_1 = C_2H_5 ; X = CH_3	2.58, 3.58	2.65	4.52	7.50	7.96 - 8.65	1.91	3.86
Compound 9 R_1 = C_3H_8 ; X = CH_3	1.83, 3.86, 4.04	2.54	4.25	7.61	7.99 - 8.23	1.80	3.91

3.3. ^{13}C NMR Spectra

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

A comparative study of ^{13}C NMR Spectra of all these Chloro-bismuth(III) (heteroleptic) derivatives with their corresponding β-ketiminates exhibit carbon signals for C-OH (C^3) and imine (C^2) (C=N) carbons at and δ 162.70-168.09 and δ 190.27–186.50 respectively. The position of these carbon signals are de-shielded on complexation as compared to their signal position in the free β-ketiminates moiety. This confirms the chelation of antimony 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 53.44-52.27 and phenyl carbons of β-ketiminate moiety are appeared in the region δ 160.69 - 144.83, δ 134.52 - 128.08, δ 145.65 – 133.72, δ 130.98-126.71 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 Chlorobismuth(III)(heteroleptic) derivatives with their corresponding sodium salt of piperidine dithiocarbamate moiety indicates the remarkable upfield shift of (~~ 15-20 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-bismuth (III) heteroleptic derivatives have been appeared at their expected position as shown in Table 2.

Table 2: ^{13}C NMR Spectral Data (δ) of Chloro-Bismuth(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	Bi-Ph	C_a	C_b	C_c	C_d
Compound 1 R_1=CH_3 ; X = H	187.15	170.40	164.10	150.10	140.01	129.11	126.04	96.10	52.94	-	153.59,147.82 129.18,127.97	24.15	25.19	51.90	196.81
Compound 2 R_1=C_2H_5 ; X = H	193.78	168.25	162.10	158.01	139.81	132.58	129.79	98.10	53.69	-	153.36,142.10 129.08,127.91	24.14	25.69	53.02	199.54
Compound 3 R_1 =C_3H_8 ;X = H	189.43	170.89	163.79	160.61	145.65	129.73	126.05	98.14	60.74	-	153.15,145.22 129.62,128.70	26.63	38.31	53.24	190.28
Compound 4 R_1 =CH_3;X = -Cl	191.34	178.04	168.04	160.07	138.78	129.80	128.28	97.36	62.56	-	153.72,149.45 129.65,128.81	26.62	38.37	42.16	197.09
Compound 5 R_1=C_2H_5; X= -Cl	189.56	180.02	167.13	160.11	140.06	131.19	130.82	97.10	60.13	-	154.69,137.81 134.05,128.21	24.26	37.11	49.10	195.13
Compound 6 R_1=C_3H_8: X= -Cl	186.77	168.27	163.27	151.91	140.12	132.68	129.27	96.79	54.27	-	157.35,137.66 133.52,127.29	28.63	34.12	59.58	196.38
Compound 7 R_1=CH_3;X =CH_3	191.10	169.26	162.70	164.59	138.72	127.57	127.05	97.89	54.05	21.03	156.95,137.95 134.24,128.71	26.02	39.36	56.89	199.52
Compound 8 R_1=C_2H_5;X=CH_3	190.67	170.27	168.09	151.11	137.72	129.72	127.20	96.36	52.56	24.13	156.96,137.38 135.66,127.40	26.89	36.70	54.42	199.05
Compound 9 R_1=C_3H_8;X=CH_3	190.17	169.10	164.98	149.43	137.17	129.04	125.71	94.72	51.44	24.97	154.18,143.29 131.18,129.89	24.52	34.12	54.13	199.32

Table 3: Synthetic and Analytical Data of Chloro-Bismuth(III) (Heteroleptic) Derivatives

Complex	Reactant (gm) /m ml				% Yields empirical formula	Nacl (g) Found (Calc)	Analysis		Molecular weight Found (Calc)
	Sodium Salt of Ligands		$BiCl_3$				Bi% Found (Calc)	S % Found (Calc)	
	L_1H	L_2Na	$BiCl_3$	L_1BiCl_2					
Compound 1 R_1 = CH_3 ; X = H	0.87/1.39	0.58/0.93	1.26/2.02	1.17/1.87	76 $C_{18}H_{22}BiO_3S_2N_2Cl$	0.70 (0.65)	33.70 (33.55)	10.29 (10.90)	623.20 (622.90)
Compound 2 R_1 = C_2H_5; X = H	0.91/1.42	0.57/0.81	1.23/1.94	1.60/2.51	79 $C_{19}H_{24}BiO_3S_2N_2Cl$	0.71 (0.67)	33.20 (32.80)	10.06 (10.30)	637.20 (636.80)
Compound 3 R_1 = C_3H_7 ; X = H	0.93/1.43	0.56 / 0.86	1.19 / 1.83	1.61/2.47	72 $C_{20}H_{26}BiO_3S_2N_2Cl$	0.73 (0.70)	32.89 (32.02)	9.85 (10.10)	651.20 (650.80)
Compound 4 R_1 = CH_3 ; X = -Cl	0.95/1.44	0.55/0.83	1.18/1.79	1.62/2.46	74 $C_{18}H_{21}BiO_3N_2S_2Cl_2$	0.65 (0.61)	31.64 (32.20)	9.75 (10.02)	658.30 (657.25)
Compound 5 R_1 = C_2H_5 ; X = -Cl	0.97/1.44	0.54/0.80	1.15/1.79	1.62/2.46	79 $C_{19}H_{23}BiO_3N_2S_2Cl_2$	0.70 (0.65)	31.11 (32.08)	9.55 (9.90)	672.10 (671.20)
Compound 6 R_1 = C_3H_7 ; X = -Cl	1.00/1.45	0.53/0.77	1.12/1.63	1.63/2.37	71 $C_{20}H_{28}BiO_3S_2N_2Cl_2$	0.72 (0.66)	30.49 (31.05)	9.35 (9.70)	686.40 (685.10)
Compound 7 R_1 = CH_3 ; X = CH_3	0.91/1.42	0.57/0.89	1.23/1.92	1.60/2.50	68 $C_{19}H_{24}BiO_3S_2N_2Cl$	0.74 (0.64)	32.76 (33.12)	10.05 (10.80)	638.40 (637.20)
Compound 8 R_1 = C_2H_5 ; X = CH_3	1.01/1.54	0.56/0.85	1.19/1.88	1.60/2.50	71 $C_{20}H_{26}BiO_3S_2N_2Cl$	0.70 (0.62)	32.05 (32.90)	9.83 (10.25)	652.20 (651.70)
Compound 9 R_1 = C_3H_7 ; X = CH_3	1.02/1.53	0.55/0.82	1.16/1.74	1.62/2.43	69 $C_{21}H_{28}BiO_3S_2N_2Cl$	0.69 (0.60)	31.08 (31.80)	9.63 (10.05)	666.30 (665.80)

3.4. ESI-Mass Spectra

ESI-Mass Spectral data of one of the synthesized complexes namely Chloro-bismuth(III) (heteroleptic) derivatives have been recorded which exhibit monomeric in nature and revalent mass spectral peaks along with their relative abundance and possible fragmentation patterns are being summarized in Table 4.

Table 4: ESI-Mass Fragmention Mode of Compounds

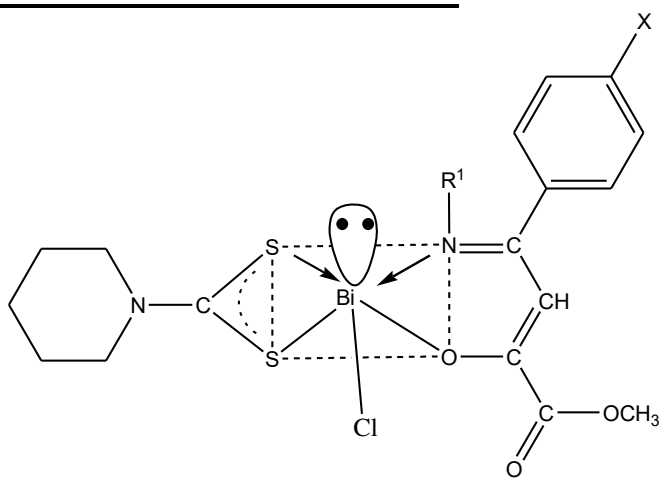
S.No.	Assignment	Mass No.	Relative abundance %
1.	$(Cl)BiO_3S_2N_2C_{18}H_{22}^{+}$	622.80	12.01/15.50
2.	$(Cl)BiO_3SC_{18}H_{22}^{+}$	562.70	21.32/ 15.30
3.	$(Cl)BiSC_{10}H_{14}^{+}$	420.60	100
4.	$(Cl)BiSC_7H_4^{+}$	374.60	5.65/16.23
5.	$(Cl)BiSC_2H_2^{+}$	315.50	9.30/15.20
6.	$Bi\text{-}S^{+}$	241.10	27.10/35.20

As we know compound containing one chlorine atom exhibits isotope peaks along with molecular ion peak M^+ and M^{+2}. The molecular ion peaks (M^+ and M^{+2}) each contains one chlorine atom but the chlorine can be either of the two chlorine isotopes ^{35}Cl and ^{37}Cl and hence two line at m/z 623.10 and m/z 621.80 with peak height in the ratio 3:1 are observed in the case.

3.5. Structure Ecludation

The molecular structure of these Chloro-bismuth(III) (heteroleptic) derivatives in which bismuth 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 [23]. 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-bismuth(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 bismuth atom in bidentate manner. Therefore the following structures in which bismuth atom acquires distorted octahedral geometry having stereo-chemical active lone pair of electron may be assigned for Chloro-bismuth(III) (heteroleptic) derivatives having β-ketiminates and piperidine dithiocarbamate.



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

3.6. Biological Activity

Heteroleptic derivatives of Chlorobismuth (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 [24]. The results indicate that 1-6 > L_1- L_{10} the data are summarized in Table 5 and 6.

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	08	19	20	16	12	14	17	12	21
P.Funiculosum(fungi)	20	02	22	08	14	19	17	07	16	16
Fusarium (fungi)	22	21	08	09	12	07	11	20	13	19
B.Subtalis (bacteria)	17	03	19	20	07	15	08	13	15	14
P.Aeruginosa (bacteria)	05	12	15	08	14	12	14	07	09	19
E.Coli (bacteria)	15	00	20	12	17	05	11	15	17	15

Table 6: Inhibition Zone of Chloro-bismuth(III) (Heteroleptic) Derivatives against Bacteria and Fungi

Microorganisms	Compounds								
	1	2	3	4	5	6	7	8	9
T. Resei (fungi)	15	03	09	17	18	15	09	12	09
P.Funiculosum(fungi)	09	08	06	22	15	09	17	15	12
Fusarium (fungi)	14	18	10	18	07	03	14	09	14
B. Subtalis (bacteria)	12	10	06	09	17	10	09	08	09
P.Aeruginosa (bacteria)	02	07	18	08	20	06	06	20	18
E.Coli (bacteria)	09	09	08	03	11	15	10	13	10

4. ACKNOWLEDGEMENT

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