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RESEARCH ARTICLE

SYNTHESIS, SPECTRAL STUDIES AND ANTIMICROBIAL ACTIVITY OF ARSENIC (III) BENZOYL AND P-SUBSTITUTED BENZOYL PIPERIDYL THIOCARBAMYLS

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ABSTRACT

Dichloroarsenic (III) benzoyl and p-substituted benzoyl piperidyl thiocarbamyl and Chloroarsenic (III) di benzoyl and p-substituted di benzoyl piperidyl thiocarbamyls of the type $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$ have been synthesized in acetone by the reaction of $AsCl_3$ and benzoyl and p-substituted benzoyl piperidyl thiocarbamyls in 1:1 and 1:2 molar ratios at room temperature [$C_{13}H_{14}N_2OSX$, X= H in compound 1,5, OCH_3 in 2,6, OH in 3,7 and Cl in 4,8 respectively]. These newly synthesized derivatives have characterized by elemental analysis (C, H, N, Cl, S, O and As), molecular weight measurements and spectral (IR, ^{1}H NMR, ^{13}C NMR) studies. All compounds screened against different bacteria and fungi show moderate antibacterial and antifungal activities.

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INTRODUCTION

Arsenicals have been used since ancient Greek and Roman civilizations and in the Far East as part of traditional Chinese medicine. In Western countries, they became a therapeutic mainstay for various ailments and malignancies in the 19th and early 20th centuries (Thomas *et al*., 2009). Arsenic (III) has a considerable affinity for charged O or S donor ligands, the latter including dithioacid chelates, but complexes with neutral O and S donor ligands are much rare. Crown ether adducts are also characterized by usually ring As-O bonds(Alcock *et al*., 1993 and Borgsen *et al*., 1990). Arsenic (III) tripyrazolinates have been synthesized by the reaction of $AsCl_3$ and sodium salt of pyrazolines in 1:3 molar ratios in anhydrous benzene at elevated temperature. And found greater activity of arsenic (III) tripyrazolinates towards all tested bacteria than free pyrazoline (Tripathi *et al*., 2009). N-(2-phenylethyl) piperidine-1-carbothioamide has been synthesized and evaluated anti-oxidant activity & found more active compounds among other heterocycle based thioureas (Venkatesh *et al*., 2009). In the present article, we described the syntheses, spectral study and antimicrobial activity of arsenic (III) benzoyl & p-substituted benzoyl piperidyl thiocarbamyls. The combination of arsenic (III) with thiocarbamyls provides complexes with good effectiveness against bacteria and fungi.

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Experimental

Solvents (benzene, acetone and alcohol) were rigorously dried and purified by standard methods before use (Brian *et al*., 1989). All chemicals were of analytical grade. Arsenic trichloride was prepared in laboratory by the reaction of arsenic trioxide with thionyl chloride (Tripathi *et al*., 2004), and Piperidine (CDH) is used as received.

Synthesis of ligands

Synthesis of benzoyl piperidyl thiocarbamyl

Benzoyl chloride (0.5 mol) and ammonium thiocynate (0.5 mol) dissolved in acetone (20 ml) separately and both the solutions cooled to 0°C on Ice bath. These solutions were mixed drop by drop with constant stirring the white precipitate of ammonium chloride was formed and solution developed pink color. The reaction mixture was then heated for a few minutes to complete the reaction. The solution was filtered through the glass wool to get benzoyl isothiocynate (Robert *et al*., 1948). Benzoyl isothiocyanate oil (0.5 mol) was added drop by drop with constant shaking to a solution of piperidine (0.5 mol) in benzene (30 ml) at temperature 30-40 °C. The solution was warmed for 10 minutes. On scratching with a glass rod a crystalline residue was obtained. The precipitate was filtered, washed with benzene and was recrystallised from ethanol.

Synthesis of p-substituted benzoyl piperidyl thiocarbamyl

p-substituted benzoyl chloride (0.5 mol) (substituents are –OCH_3, –OH & –Cl and ammonium thiocynate (0.5 mol) dissolved in acetone separately and both the solutions cooled to 0°C on ice bath. These solutions were mixed drop by drop with constant stirring the white precipitate of ammonium chloride was formed and solution developed pink color. The reaction mixture was then heated for a few minutes to complete the reaction. The solution was filtered through the glass wool to get p-substituted benzoyl isothiocynate. p-substituted benzoyl isothiocyanate oil (0.5 mol) was added drop by drop with constant shaking to a solution of piperidine (0.5 mol) in benzene (30 ml) at temperature 30-40 °C. The solution was warmed for 10 minutes. On scratching with a glass rod a crystalline residue was obtained. The precipitate was filtered, washed with benzene and was recrystallised from ethanol.

Synthesis of Complexes

Synthesis of $AsCl_2(C_{13}H_{14}N_2OSX)$

New complexes of the type dichloroarsenic (III) benzoyl and p-substituted benzoyl piperidyl thiocarbamyls $AsCl_2(C_{13}H_{14}N_2OSX)$ were synthesized by the reaction of thiocarbamyls and $AsCl_3$ in 1:1 molar ratios at room temperature.

$$AsCl_3 + 2(C_{13}H_{15}N_2OSX) \xrightarrow{\text{Acetone}} AsCl(C_{13}H_{14}N_2OSX)_2 + 2HCl$$

The acetone solution of benzoyl and p-substituted benzoyl piperidyl thiocarbamyls was mixed with acetone solution of $AsCl_3$ with constant stirring and the reaction mixture further stirred for 2 hours at room temperature till the color of the reaction mixture underwent a change. Reaction mixture was filtered the solvent was removed under reduced pressure from the filtrate. The yellow colored solid obtained was repreceipted in acetone and dried by vacuum to get the purified product. (Analytical results were presented in Table 1) Compounds 1, 2, 3 & 4 were prepared by the same route.

Synthesis of $AsCl(C_{13}H_{14}N_2OSX)_2$

New complexes of the type chloroarsenic (III) di (benzoyl and p-substituted benzoyl piperidyl thiocarbamyls $AsCl(C_{13}H_{14}N_2OSX)_2$ were synthesized by the reaction of $AsCl_3$ and thiocarbamyls in 1:2 molar ratios at room temperature.

$$AsCl_3 + 2(C_{13}H_{15}N_2OSX) \xrightarrow{\text{Acetone}} AsCl(C_{13}H_{14}N_2OSX)_2 + 2HCl$$

The acetone solution of benzoyl and p-substituted benzoyl piperidyl thiocarbamyls was mixed with acetone solution of $AsCl_3$ with constant stirring and the reaction mixture further stirred for 2 hours at room temperature till the color of the reaction mixture underwent a change. Reaction mixture has filtered the solvent was removed under reduced pressure from the filtrate. The yellow colored solid obtained was repracipited in acetone and dried by vacuum to get the purified product. (Analytical results were presented in Table 1) Compounds 5, 6, 7 & 8 were prepared by the same route.

Physical Measurements

Chlorine was estimated by Volhard's method (Chauhan *et al*., 1983). And arsenic was estimated iodometrically (Vogel *et al*., 1989). Infrared spectra were recorded on a Perkin Elmer Model 557 FT-IR spectrophotometer using a CsI cell from 4000-200 cm^{-1}, NMR spectra were recorded at room temperature on Bruker DRX-300 spectrometer operated at 300 and 75.45 MHz for ^1H and (Piddock *et al*., 1990). C using TMS (tetramethylsilane) as internal standard. Molecular weights were determined on a Knauer Vapor pressure (Muller *et al*., 1979 and Chordia *et al*., 2008) in $CHCl_3$ at 45°C. The elemental analysis (C, H and N) was estimated by Coleman C, H, N analyzer.

Antimicrobial Studies

Agar disc diffusion technique was used for screening in vitro antimicrobial activity (Piddock *et al*., 1990; Wayne *et al*., 2002 and Davidson *et al*., 2005) Inoculums of bacteria were prepared in nutrient broth and fungi in potato dextrose agar slant.

Table 1. Analytical and physical data for $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$ complexes

S. No	Product	Yield %	M.P. °C	Elemental Analysis % (Calculated) Found							M.W. (Calc) Found
				C	H	N	O	S	Cl	As	
1	$AsCl_2(C_{13}H_{14}N_2OSX)$	82	278	(37.04)	(41.30)	(4.21)	(6.88)	(3.93)	(7.87)	(17.41)	(407.19)
				36.6	42.05	4.33	6.53	3.43	7.62	17.89	406.98
2	$AsCl_2(C_{13}H_{14}N_2OSX)$	81	282	(37.22)	(41.21)	(4.38)	(6.41)	(7.32)	(7.33)	(16.22)	(437.22)
				36.63	41.82	4.22	7.04	7.2	6.42	16.67	437.64
3	$AsCl_2(C_{13}H_{14}N_2OSX)$	79	195	(35.77)	(39.73)	(4.05)	(6.62)	(7.56)	(7.58)	(16.76)	(423.19)
				36.52	39.29	4.24	6.17	8.06	7.48	16.66	423.51
4	$AsCl_2(C_{13}H_{14}N_2OSX)$	80	190	(34.42)	(38.07)	(3.65)	(6.34)	(3.62)	(7.26)	(24.08)	(441.64)
				33.98	37.17	3.55	6.84	4.02	7.45	24.58	442.05
5	$AsCl(C_{13}H_{14}N_2OSX)_2$	77	218	(49.46)	(53.12)	(5.41)	(8.85)	(5.05)	(10.13)	(5.60)	(633.10)
				49.96	52.68	5.6	8.4	5.55	10.03	5.5	633.29
6	$AsCl(C_{13}H_{14}N_2OSX)_2$	75	243	(48.69)	(51.98)	(5.53)	(8.08)	(9.23)	(9.25)	(5.11)	(693.15)
				47.79	52.48	5.43	8.27	9.63	8.8	5.01	692.26
7	$AsCl(C_{13}H_{14}N_2OSX)_2$	69	162	(47.24)	(50.56)	(5.15)	(8.42)	(9.62)	(9.64)	(5.33)	(665.10)
				47.85	49.97	5.55	8.61	10.12	9.54	4.43	664.78
8	$AsCl(C_{13}H_{14}N_2OSX)_2$	77	179	(44.91)	(47.91)	(4.59)	(7.98)	(4.56)	(9.14)	(15.15)	(701.99)
				44.32	47.32	4.99	8.17	5.06	9.04	14.25	701.16

Where X=H in 1and 5; OCH_3 in 2 and 6; OH in 3 and 7 and Cl in 4 and 8.

The culture were inoculated and incubated for 24 h in case of bacteria and 72 hours for fungi. Molten medium was poured in a sterile petri dish (9 cm in diameter) to get a depth of 5 mm. The medium was left to solidify and then seed with respective test organisms. For the purpose of seeding to get suspension of fungi spore. A Sterile cotton swab was dipped in the culture/ suspension and lightly rubbed over the solidified medium. The plate was left for a few minutes and then used for the test. 30 µm of each sample to be tested was dissolved in 1ml acetone article discs (5 mm disc of Whatmann filter paper article no. 42 cut and sterilized) were immersed in solution of sample, removed and left in a sterile Petri dish to permit the solvent to evaporate. After 10 min the article discs were transferred to seeded agar plates. The dishes were incubated at 37°C for 24 hours (for bacteria) and at 30°C for 72 hours (for fungi), where clear inhibition zones were detected around each disc. A disc soaked in acetone alone was used as a control under the same conditions and there was no inhibition zone. Each distinct inhibition zone was measured as diameter in mm, both antibacterial and antifungal activity was calculated as a mean of three replicates.

RESULT AND DISCUSSION

General Properties

All the compounds are yellow colored amorphous solids and stable at room temperature. These are partially soluble in organic solvents (chloroform and ether) and soluble in coordinating solvents (tetrahydrofuran, dimethylformamide and dimethylsulphoxide). The molecular weight measurement in dilute chloroform solution at 45°C shows monomeric nature of these compounds. The elemental analysis of (C, H, N, S, O, Cl and As) data is in accordance with stochiometry proposed for respective compounds.

I R Spectra

The infrared spectral data summarized in Table 2. The N–H stretching vibrations at 3210-3250 cm^{-1} in free ligands disappear in the complexes mainly due to the loss of the proton from acyl-substituted nitrogen of ligand upon forming the neutral complexes (Gulten *et al*., 2009; Nguyen *et al*., 2009; El-Shazly *et al*., 2000 and Zhang *et al*., 2007). The band 1691-1721cm^{-1} is assigned to C=O stretching vibrations in the ligands but in the complexes, it is disappeared (Nguyen *et al*., 2009 and Nguyen *et al*., 2007) The C=S vibration at ~1280 cm^{-1} for free ligands is shifted to ~1230 cm^{-1} (Zhang *et al*., 2007; Nguyen *et al*., 2007 and Nguyen *et al*., 2009). This indicates coordination of the metal by S and O atoms. Aromatic C–H stretching vibrations at 3102-3179 cm^{-1} (Saeed *et al.,* 2010) and aromatic C=C stretching are observed at 1563-1613 cm^{-1} whereas C=N stretching is observed at 1529-1568 cm^{-1}. New bands appearing at 444-452 cm^{-1} and 338-357 cm^{-1} are attributed to As–O and As–S stretching vibrations (El-Shazly *et al*., 1999; Gulten *et al*., 2009; Silverstein *et al*., 1981).

Multinuclear NMR Studies

The ^{1}H NMR data of complexes are summarized in Table 3. All the proton signals of the ligands shift to lower fields upon binding to metal ions. Ligands show a peak at δ 8.14 - 8.45 ppm respectively corresponding to the proton of the N-H group. This peak does not appear in the complexes that contain the deprotonated ligand, indicating the imine linkage in these complexes. The NH signal disappears in the spectra of the metal complexes indicating the chelation of the ligand moiety to arsenic through the oxygen & sulphur atom.

Table 2. IR spectral data (cm^{-1}) for data for $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$ complexes

S.No	Compounds	ν(C–H)	ν(C=C)	ν(C=S)	ν(C=N)	ν(C–O)	ν(As–S)	ν(As–O)
1.	$AsCl_2(C_{13}H_{14}N_2OSX)$	3132	1598	1234	1560	1231	361	428
2.	$AsCl_2(C_{13}H_{14}N_2OSX)$	3112	1597	1231	1554	1226	350	425
3.	$AsCl_2(C_{13}H_{14}N_2OSX)$	3134	1600	1237	1545	1226	356	419
4.	$AsCl_2(C_{13}H_{14}N_2OSX)$	3151	1579	1256	1555	1243	355	415
5.	$AsCl(C_{13}H_{14}N_2OSX)_2$	3135	1601	1236	1556	1237	359	423
6.	$AsCl(C_{13}H_{14}N_2OSX)_2$	3107	1605	1227	1561	1227	344	421
7.	$AsCl(C_{13}H_{14}N_2OSX)_2$	3141	1603	1240	1537	1229	352	410
8.	$AsCl(C_{13}H_{14}N_2OSX)_2$	3165	1571	1268	1551	1254	352	405

Where X=H in 1 and 5; OCH_3 in 2 and 6; OH in 3 and 7 and Cl in 4 and 8.

Table 3. ^{1}H NMR spectral data for $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$ complexes

S. No.	Chemical Shift (in δ ppm)
1.	7.51-7.91 (5H, m, Ar–H); 3.11 (4H, t, CH_2); 1.54 (4H, m, CH_2); 1.61 (2H, m, CH_2)
2.	7.15-8.1 (4H, m, Ar–H); 3.12 (4H, t, CH_2); 1.56 (4H, m, CH_2); 1.52 (2H, m, CH_2); 3.84 (3H, s, OCH_3)
3.	6.87-7.99 (4H, m, Ar–H); 3.17 (4H, t, CH_2); 1.59 (4H, m, CH_2); 1.62 (2H, m, CH_2); 5.40 (1H, s, OH)
4.	7.42-7.87 (4H, m, Ar–H); 3.20 (4H, t, CH_2); 1.55 (4H, m, CH_2); 1.59 (2H, m, CH_2)
5.	7.51-7.91 (10H, m, Ar–H); 3.11 (8H, m, CH_2); 1.51 (8H, m, CH_2); 1.56 (4H, m, CH_2)
6.	7.16-8.5 (8H, m, Ar–H); 3.12 (8H, m, CH_2); 1.54 (8H, m, CH_2); 1.61 (4H, m, CH_2); 3.86 (6H, m, OCH_3)
7.	6.85-7.96 (8H, m, Ar–H); 3.16 (8H, m, CH_2); 1.58 (8H, m, CH_2); 1.64 (4H, m, CH_2); 5.40 (2H, m, OH)
8.	7.50-7.77 (8H, m, Ar–H); 3.18 (8H, m, CH_2); 1.57 (8H, m, CH_2); 1.68 (4H, m, CH_2)

Where X=H in 1 and 5; OCH_3 in 2 and 6; OH in 3 and 7 and Cl in 4 and 8, m=multiplet, s=singlet, t=triplet.

Table 4. ^{13}C NMR spectral data for $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$complexes

S. No.	Chemical Shift (in δ ppm)
1.	128.1- 131(Ar–C); 52.5 (CH_2); 25.4 (CH_2); 24.1 (CH_2); 152.4 (C=N); 181.1 (C=S)
2.	114.6- 129.5 (Ar–C); 161.8 (Ar–OCH_3); 52.4 (CH_2); 25.7 (CH_2); 24.8 (CH_2); 56.9 (O-CH_3); 158.1 (C=N); 183.4 (C=S)
3.	116- 130.6 (Ar–C); 160.8(Ar–OH); 52.3 (CH_2); 25.6 (CH_2); 24.5 (CH_2); 152.8 (C=N); 181.7 (C=S)
4.	125.2- 128.3 (Ar–C); 137.3 (Ar–Cl); 53.1 (CH_2); 23.4 (CH_2); 25.1 (CH_2); 154.7 (C=N); 183.1 (C=S)
5.	128.05- 131(Ar–C); 52.3 (CH_2); 25.6 (CH_2); 24.5 (CH_2); 152.8 (C=N); 165.9 (C=S)
6.	115.1- 131.2 (Ar–C); 160.4 (Ar–OCH_3); 52.7 (CH_2); 25.9 (CH_2); 24.1 (CH_2); 55.6 (O-CH_3); 155.1 (C=N); 162.2 (C=S)
7.	115- 131.2 (Ar–C); 161.1 (Ar–OH); 52.4 (CH_2); 25.7 (CH_2); 24.3 (CH_2); 151.9 (C=N); 169.1 (C=S)
8.	128.1- 129.9 (Ar–C); 137.1 (Ar–Cl); 53.1 (CH_2); 26.1 (CH_2); 23.4 (CH_2); 153.2 (C=N); 169.6 (C=S)

Where X=H in 1 and 5; OCH_3 in 2 and 6; OH in 3 and 7 and Cl in 4 and 8.

The spectra of the complexes exhibit aromatic proton signals in the range of δ 6.85-8.5 ppm (Silverstein *et al*., 1981; Duan *et al*., 2010) and piperidyl –CH_2 proton signals in the range of δ 1.51-3.18 ppm (Sharma *et al*., 2004; Cholli *et al*., 1993). The (Piddock *et al*., 1990) ^{13}C NMR data of complexes are summarized in Table 4. A comparison of spectra of the metal complex with those of the ligands provide very useful information about the mode of bonding. The signal for C=N carbon appears at δ 152.8-153.6 ppm in complex but it was not observed in free ligand. The signal for C=S carbon appearing at ~ δ 178.2 is shifted to ~ δ 171.2 ppm in complexes. This indicates that O & S atoms are involved in chelate formation. The signals for aromatic carbon appear at δ 114.5- 130.6 ppm (Sudha *et al*., 1986; Wawer *et al*., 1993) and piperidyl carbon at δ 24.1- 53.1 ppm (Ernest *et al*., 1980).

Structure

The bidentate behavior $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$ is indicated by IR, ^1H NMR and ^{13}C NMR data. In complexes $AsCl_2(C_{13}H_{14}N_2OSX)$ the central arsenic (III) atom appears to acquire the coordination number four and most plausible geometry around arsenic atom is distorted trigonal bipyramidal [Figure 1 (a) including lone pair of electron]. In complexes AsCl $(C_{13}H_{14}N_2OSX)_2$ the central arsenic (III) atom appears to acquire the coordination number five and most plausible geometry around arsenic atom is distorted octahedral [Figure 1 (b) including lone pair of electron]

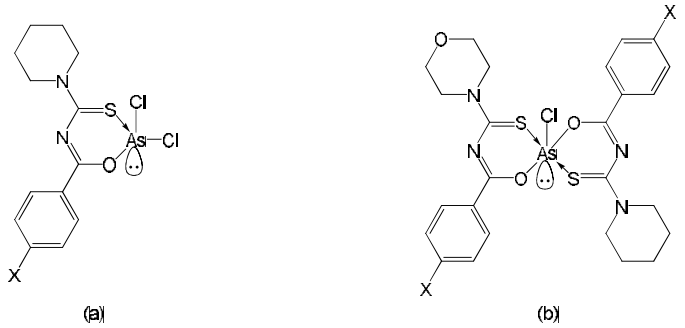

Figure 1. Structure of $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$

Microbial Assay

The antimicrobial activity of free ligands and complexes were tested against the bacterial species Stephylococcus aureus, Bacillus lichaniformis, Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa and Vibrio spp and the antifungal activity were tested against Aspergillus niger and Penicillium notatum. The antimicrobial activity of some antibiotics viz. chloramphenicol and terbinafin were also tested and compared with free ligands and their arsenic (III) complexes. The results are listed in Table 5.

Table 5. Antimicrobial activities of free thiocarbamyls and arsenic (III) thiocarbamyls

S.No.	Free ligands and their metal complexes	Zone of inhibitions in mm.							
		Bacteria						Fungi	
		E. coli	B. lichaniforms	P. aeruginosa	V.ssp.	K. pneumoniae	S. aureus	P. notatum	A. niger
1	($C_{13}H_{15}N_2OSX$)	12	11	13	12	17	12	11	15
2	($C_{13}H_{15}N_2OSX$)	11	10	13	14	12	11	13	14
3	($C_{13}H_{15}N_2OSX$)	10	12	13	12	14	11	10	15
4	($C_{13}H_{15}N_2OSX$)	11	11	12	10	13	14	13	09
5	$AsCl_2$ ($C_{13}H_{14}N_2OSX$)	13	12	12	12	15	13	12	16
6	$AsCl_2$ ($C_{13}H_{14}N_2OSX$)	13	14	15	15	13	14	14	16
7	$AsCl_2$ ($C_{13}H_{14}N_2OSX$)	13	16	15	18	17	13	12	15
8	$AsCl_2$ ($C_{13}H_{14}N_2OSX$)	13	13	14	14	16	15	14	12
9	AsCl $(C_{13}H_{14}N_2OSX)_2$	15	13	14	13	17	14	13	17
10	AsCl $(C_{13}H_{14}N_2OSX)_2$	14	16	17	15	14	14	15	18
11	AsCl $(C_{13}H_{14}N_2OSX)_2$	15	18	18	17	19	14	12	15
12	AsCl $(C_{13}H_{14}N_2OSX)_2$	14	16	15	17	18	17	14	13
13	R	23	24	24	24	24	24	25	24

X= H in1, 5 and 9, X= OCH_3 in 2, 6 and 10, X= OH in 3,7 and 11, X= Cl in 4,8 and 12

R= Chloramphenicol (antibacterial agent), Terbinafin (antifungal agent).

Conclusion

It is observed that complexation of free ligands with arsenic trichloride in all proportions increases the antimicrobial activities. That's why $AsCl_2(C_{13}H_{14}N_2OSX)$ and $AsCl(C_{13}H_{14}N_2OSX)_2$ exhibited higher antimicrobial activities as compared to free ligands but in comparison to antibiotics all the complexes showed moderate antimicrobial activities.

Chloroarsenic (III) p-substituted benzoyl thiocarbamyls shows more activity than dichloroarsenic (III) p-substituted benzoyl thiocarbamyls.

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