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Synthesis and spectral studies of organoarsenic(III) complexes of Schiff bases

Rita Gupta

Pt. N. K. S. Govt. P.G. College Dausa, **INDIA**

Email: ritagupta16@rediffmail.com

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ABSTRACT

Some phenylarsenic(III) Schiff base complexes of the type $PhAs[OC(R)CHC(R')NC(R'')]_nCI_{2-n}$ *(where n =1 or 2,*$R=CH_3$,$R'=C_6H_5$,$R'= -H_2CH_2$, $-HCH_2C_6H_5$; $R=R'=C_6H_5$,$R''= -H_2CH_2$, $-HCH_2C_6H_5$*) have been prepared by the reaction of* $PhAsCl_2$ *with sodium salt of Schiff base in 1: 1 and 1: 2 molar ratios in anhydrous benzene. These compounds have been characterized by elemental analyses, molecular weight measurement, IR, and multinuclear NMR (*^1H & ^{13}C*) spectroscopy. Antibacterial and antifungal potential of Schiff base and their corresponding phenyl arsenic (III) derivatives have also discussed.*

Keywords: Phenylarsenic (III), Schiff base, spectroscopy, Antibacterial, Antifungal.

INTRODUCTION

Arsenic is the 33rd element with higher toxicity [1] as well as higher bioavailability in the periodic table. Arsenic compounds are used effective antibacterial drugs [2-3] to treat a variety of diseases including syphilis [4] and cancer [5]. Interest in organoarsenic compounds is due to their wide ranging applications in biocidal activities. The trivalent compounds show a considerable structural diversity which is extended by the presence of a stereochemically active lone pair of electron [6,7].

Schiff bases represent one of the most widely utilized class of ligands in metal coordination chemistry. It has been reported that metal complexes of amino acid shiff bases possess anticarcinogenic activity [8,9] and interesting feature of their coordination behavior[10,11].

Although, organoarsenic (III) complexes of Schiff bases have been reported [12-14] but no reports about the amino acid derived Schiff bases are available. In view of this and in pursuance of our work [15] on organometallic complexes of group 15 we have prepared phenylarsenic (III) Complexes of Schiff bases derived from amino acid.

MATERIALS AND METHODS

All the reactions were carried out under moisture free environment and solvents were dried by standard procedure [16]. Phenylarsenic (III) dichloride [17] and Schiff base [11] have been synthesized by the

literature method. Arsenic, nitrogen, and chlorine were estimated by iodometrically, gravimetric and Volhard's methods, respectively [18].

IR Spectra of these compounds were recorded as Nujol mull using KBr cells in the range 4000-400 cm^{-1} on FT-IR spectrophotometer model 8400 S Shimadzu. The NMR (^{1}H and ^{13}C NMR) spectra have been recorded on JEOL-FTAL 300 MHz spectrometer in $CDCl_3$ solution using TMS as an internal reference. The elemental analysis (C, H & N) was obtained by using a Perkin Elmer 2400 CHN analyzer.Molecular weights were deterimined cryoscopically in freezing benzene solution using a Beckmann's thermometer. Since similar methods have been used to synthesize these compounds, the preparation of only one complex is being described here and the analytical results are being summarized in tables.

Synthesis of $PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]_2$: A benzene solution of $CH_3C(O)$ CHC $(C_6H_5)N(H)CH_2CH_2COOH$ (1.11 g; 4.66 mM) was added to sodium methoxide solution. The reaction mixture was refluxed for 2 h, giving a yellow colourd solution. The benzene solution of $PhAsCl_2$ [0.53 gm, 2.32 mM] was added to the above reaction mixture after cooling. The reaction mixture was further stirred at room temperature for 4 h till the colour of mixture became dark yellow and the precipitated NaCl was filtered off. The removal of volatile component from the filtrate under reduced pressure yield a dark brown viscous, which was purified by benzene/ n-hexane mixture. The analytical results are presented in table 1.

Table 1: Synthetic & Analytical Data of Phenylarsenic (III) complexes of Schiff Base

S.No.	Na	Reactants (gm) RC(O)CHC(R')NHC(R")COOH	$PhAsCl_2$	Product % Yield	Elemental Analyses Found (Calcd.) C	H	N	As	Mol. Wt. Found (Calcd.)
1	0.11	R=CH_3,R'=C_6H_5, R"=-H_2CH_2 1.11	0.53	$C_{32}H_{33}O_6N_2As$ 82%	62.1 (62.28)	5.3 (5.35)	4.51 (4.54)	12.00 (12.16)	600 (616.5)
2	0.14	R"=-$HCH_2C_6H_5$ 1.88	0.67	$C_{44}H_{41}O_6N_2As$ 78%	68.34 (68.75)	5.21 (5.33)	3.45 (3.64)	9.38 (9.76)	750.00 (768)
3	0.12	R=R'=C_6H_5, R"=-H_2CH_2 1.54	0.58	$C_{42}H_{37}O_6N_2As$ 88%	68.00 (68.05)	4.9 (4.99)	3.71 (3.78)	10.00 (10.12)	720.00 (740.6)
4	0.11	R"=- $HCH_2C_6H_5$ 1.77	0.53	$C_{54}H_{45}O_6N_2As$ 80%	72.00 (72.64)	5 (5.04)	3.98 (3.13)	8.12 (8.91)	890.00 (897.9)

Synthesis of $PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]Cl$: A benzene solution of $CH_3C(O)CHC$ (C_6H_5) N(H) CH_2CH_2COOH [1.01 gm; 4.33 mM] was added to sodium methoxide solution. The reaction mixture was refluxed for 2 h giving a yellow coloured solution. The benzene solution of $PhAsCl_2$ [0.96 g, 4.21 mM] was added to the above reaction mixture after cooling. The reaction mixture was further stirred at room temperature for 3 h till the colour of mixture became dark yellow and the precipitated NaCl was filtered off. The removal of volatile component from the filtrate under reduced pressure yield a dark brown viscous. The product was recrystallized from n-hexane mixture. The analytical results are presented in table 2.

Table 2: Synthetic & Analytical Data of Chloro phenylarsenic (III) complexes of Schiff Base

S.No.	Na	Reactants (gm)	PhAsCl_2	Product % Yield	Elemental Analyses Found (Calcd.)					Mol. Wt. Found (Calcd.)
		RC(O)CHC(R')NHC(R")COOH			C	H	N	Cl	As	
1		R=CH_3,R'=C_6H_5, R"=-H_2CH_2		$C_{19}H_{19}O_3NAsCl$	54.12	4.49	3.23	8.12	17.02	400
	0.11	1.01	0.96	78%	(54.32)	(4.52)	(3.53)	(8.45)	(17.86)	(419.5)
2		R"=-$HCH_2C_6H_5$		$C_{25}H_{23}O_3NAsCl$	60.23	4.6	2.80	7.10	15.00	480.00
	0.09	1.20	0.87	80%	(60.50)	(4.63)	(2.82)	(7.15)	(15.12)	(495.8)
3		R=R'=C_6H_5, R"=-H_2CH_2		$C_{24}H_{21}O_3NAsCl$	59.78	4.3	2.89	7.12	15.34	470.00
	0.09	1.15	0.87	80%	(59.81)	(4.36)	(2.90)	(7.37)	(15.57)	(481.5)
4		R"=- $HCH_2C_6H_5$		$C_{30}H_{25}O_3NAsCl$	64.34	4.4	2.40	6.12	13.21	540.00
	0.10	1.61	0.96	85%	(64.57)	(4.48)	(2.50)	(6.36)	(13.44)	(557.9)

Antifungal and Antibacterial Screening: The antifungal and antibacterial activity of the parent ligand and their complexes was tested in vitro for the growth inhibiting potential against fungal (*A.niger)* and bacterial strains(*E. coli)* using Radial growth method and Paper disc technique, respectively [19].

RESULTS AND DISCUSSION

The reaction of $PhAsCl_2$with the sodium salts of Schiff base in 1:1 and 1:2 molar ratio have been carried out to yield corresponding phenylarsenic (III) derivatives.

$PhAsCl_2 + n[NaOCO(R)CHC(R^1)NC(R^{"})COOH] \rightarrow$

$PhAs[OC(R)CHC(R^{'})NC(R^{"})COOH]_nCl_{2-n}+nNaCl$

(where n =1or 2, R=CH_3,R'=C_6H_5,R"= -H_2CH_2, -$HCH_2C_6H_5$; R=R'=C_6H_5,R"= -H_2CH_2, -$HCH_2C_6H_5$)

All these derivatives are colored viscous,monomeric in nature and are soluble in common organic solvents.

I.R. Spectra: A comparative study of IR spectra of these compounds with their corresponding Schiff base shows disappearance of absorption band for -NH, observed as a broad band at 2900-3100 cm^{-1} in the spectra of free ligands, indicating the deprotonation of NH group. Appearance of a new band at around 420± 10 cm^{-1} may be attributed to νAs –N [20] stretching which also supports the bonding of central arsenic atom with nitrogen atom. The intense absorption bands observed for the free ligand in the region 1600-1610 cm^{-1} and 1560- 1570 cm^{-1} which have been assigned to νC = N and ν C = 0 are shifted to lower wave number in the spectra of their corresponding phenylarsenic (III) complexes. The shift in the position of these bands indicates involvement of these groups in bonding. The presence of another band at around 520 ± 15 cm^{-1} assigned to νAs-0[21]confirmed the chelation. Apperance of the streching frequency at 1700-1708 cm^{-1} assigned to νCOOH has been observed in the spectra of ligands as well as their corresponding organoarsenic (III) complexes. This indicates that the carboxylic group has not taken part in chelation.

^{1}H NMR Spectra: The characteristic signals in the ^{1}H NMR spectra of all these derivatives are summarized in table 3. Absence of NH signal in the region δ9.2-10.6 indicates the complexion of arsenic with schiff base through As-N bond. A small down field shift in the position of alkyl proton signal may be due to the delocalization of electrons in quasi-aromatic ring. The phenyl protons are observed as complex

pattern in the range 7.08-8.01 ppm. Apperance of COOH proton as singlet in the region 11.2 - 11.8 ppm. in the spectra of ligands and their metal complexes, further support the non involvement of COOH group on complexation.

Table 3 : ^{1}H NMR data (In ppm) of Phenylarsenic (III) Complexes of Schiff bases

S.No.	Complexes	CH_3	CH_2	CH	C_6H_5	COOH
1	a b	1.98 (S)	2.51 (t)	6.11 (s)	7.26 - 7.95 (m)	11.20 (S)
	$PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]_2$		3.28 (t)			
2	a b	1.90 (S)	2.98 (d)	6.23 (s)	7.21 - 7.90 (m)	11.5 (S)
	$PhAS[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]_2$			3.45 (t)		
3	a b	-	2.34 (t)	6.24 (s)	7.14 - 7.72 (m)	11.20 (S)
	$PhAs[OC(C_6H_5)CHC(C_6H_5)NCH_2CH_2COOH]_2$		3.31 (t)			
4	a b	-	2.34 (d)	6.12 (s)	7.34 - 8.01 (m)	12.0 (s)
	$PhAs[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]_2$			3.49 (t)		
5	a b	1.73 (S)	2.42 (t)	5.98 (s)	7.15 - 7.38 (m)	11.5 (s)
	$PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]Cl$		3.21 (t)			
6	a b	1.95 (S)	2.12 (d)	6.10 (s)	7.08 - 7.42 (m)	12.0 (S)
	$PhAS[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]Cl$			3.12 (t)		
7	a b	-	2.64 (t)	6.34 (s)	7.18 - 7.93 (m)	11.2 (S)
	$PhAs[OC(C_6H_5)CHC(C_6H_5)NCH_2CH_2COOH]Cl$		3.98 (t)			
8	a b	-	2.12 (d)	6.73 (s)	7.13 - 7.98 (m)	11.5 (S)
	$PhAs[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]Cl$			3.62 (t)		

^{13}C NMR SPECTRA: ^{13} C NMR chemical shift of these derivatives are summarized in table 4. ^{13}C NMR spectra exhibit carbon signals for C=O and C=N at 190.3-198.3 ppm and 165.1 - 169.8 ppm respectively in the organoarsenic (III) derivatives. These carbon signals show small downfield shift as compared to free ligands. This indicates involvement of these groups in bonding. Alkyl carbons shifted small downfield as compared to their position in the ligands confirm the delocalization of electron in chelate ring. The carboxylate carbon signal was observed at 172.3-174.6 ppm in the Schiff bases. This carbon signal does not show any significant shift in its position in organoarsenic (III) compounds, which rules out the possibility of involvement of this group in bonding during complexation. The signal for phenyl carbons attached to arsenic were observed in the range 126.0-140.2 ppm.

The corrected chemical shift values (δ')[22] and Hammet Taft constant (σR°)[23] were found to be in the range -1.0 to -3.8 ppm and -0.06 to -0.48 ppm, respectively. These negative values are an indication of electron release through dπ - pπ conjugation and poor donor capability of arsenic atom.

Antimicrobial Activity: When various bacterial and fungal strains were tested against the complexes they showed some potent activity. Among all these compounds tested maximum potency was exhibited by phenylarsenic(III) complex ($PhAsL_2$)(Table 5) against *E.Coli & F. Oxysporum.*

Table 4 : ^{13}C NMR data (In ppm) of Phenylarsenic (III) Complexes of Schiff base derived from Amino acids

S.No.	Complexes	CH_3	CH_2	CH	C=O	C=N	COOH	C_6H_5		δ '	σ R°
								C(i) C(O)	C(m) C(p)		
1	a b $PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]_2$	19.4	a, 39.2 b, 27.3	91.7	192.8	169.8	173.6	139.2 127.9	131.2 126.4	-1.5	-0.06
2	a b $PhAS[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]_2$	20.1	28.20	a, 90.8 b, 72.8	192.80	169.30	174.20	138.3 139.2	131.2 131.1	-3.8	-0.17
3	a b $PhAs[OC(C_6H_5)CHC(C_6H_5)NCH_2CH_2COOH]_2$	-	a, 40.1 b, 26.1	91.70	196.30	166.70	174.60	146.1 127.9	132.8 126.2	-1.7	-0.07
4	a b $PhAs[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]_2$	-	29.2	a, 90.8 b, 76.3	198.30	168.90	174.20	140.1 129.8	132.6 126.7	-3.1	-0.14
5	a b $PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]Cl$	18.60	a, 38.1 b, 26.4	90.80	191.60	168.70	173.40	138.2 127.1	131.2 126.1	-1	-0.48
6	a b $PhAS[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]Cl$	19.20	29.30	a, 91.2 b, 74.3	190.30	168.30	172.30	139.2 127.6	131.1 126.2	-1.4	-0.06
7	a b $PhAs[OC(C_6H_5)CHC(C_6H_5)NCH_2CH_2COOH]Cl$	-	a, 39.2 b, 26.2	91.80	195.4	165.10	172.30	139.2 129.7	133.6 126.8	-2.9	-0.13
8	a b $PhAs[OC(C_6H_5)CHC(C_6H_5)NCHCH_2C_6H_5COOH]Cl$	-	29.30	a, 91.8 b, 76.8	196.30	168.10	173.20	140.2 129.8	133.6 126.2	-3.6	-0.16

Table 5: Antimicrobial potential of schiff base and its corresponding phenylarsenic (iii) and chlorophenyl arsenic (iii) complexes

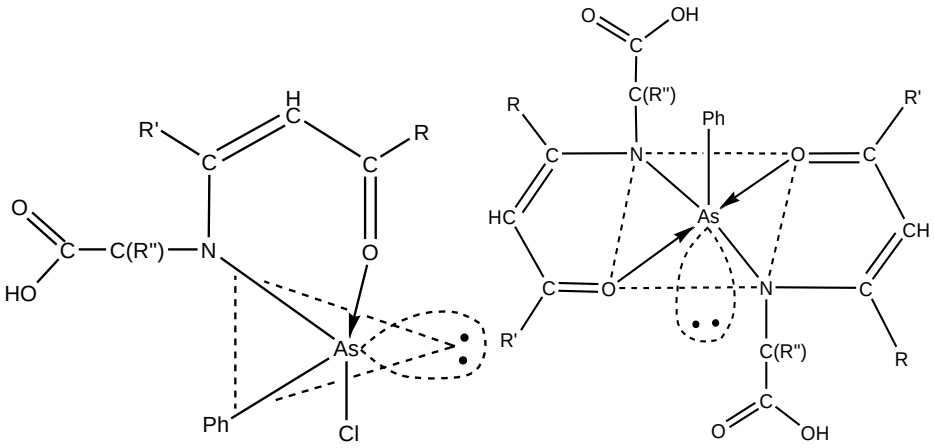
S.No.	Compound	Micro organism	600 ppm	800 ppm	1000 ppm	800 ppm	1000 ppm
1	$CH_3C[O]CHC[C_6H_5]NHCH_2CH_2COOH$; Free ligand	E Coli	20	26	22	26	22
		Pseudomonas aeruginosa	Nil	10	12	10	12
2	$PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]_2$; $PhAsL_2$	E Coli	24	28	24	28	24
		Pseudomonas aeruginosa	8	12	14	12	14
3	$PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]Cl$; PhAsLCl	E Coli	22	20	24	20	24
		Pseudomonas aeruginosa	Nil	10	12	10	12
4	$CH_3C[O]CHC[C_6H_5]NHCH_2CH_2COOH$; Free Ligand	Aspergillus Niger	24	22	28	22	28
		Fusariun Oxysporum	Nil	Nil	Nil	Nil	Nil
		Aspergillus Niger	Nil	22	24	22	24
	$PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]_2$; $PhAsL_2$	Fusariun Oxysporum	22	28	30	28	30
		Aspergillus Niger	Nil	16	20	16	20
3	$PhAs[OC(CH_3)CHC(C_6H_5)NCH_2CH_2COOH]Cl$; PhAsLCl	Fusariun Oxysporum	20	22	24	22	24

APPLICATIONS

It is difficult to make an exact structure and activity relationship between antimicrobial activity and structure of these complexes. It can possibly be concluded that the metal derivatives were found to be more inhibitory than corresponding ligand. From antimicrobial data it appears that when both chloride is replaced by schiff base, there is more significant change in antimicrobial activity as compared to chlorophenyl arsenic (III) complex and ligand. This is because of partial sharing of positive charge of metal atom with donor group which reduces the polarity of metal atom. This increases the lipophilic character of metal chelate which favour permentation through the lipid layer of cell membrane.

CONCLUSIONS

On the basis of the above spectral evidences, tetra coordinated and penta coordinated structures may be proposed for the resulting chloroorganoarsenic (III) and organoarsenic (III) complexes of schiff bases. The tentatively proposed structures of these complexes are shown in following scheme1.



Scheme1

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