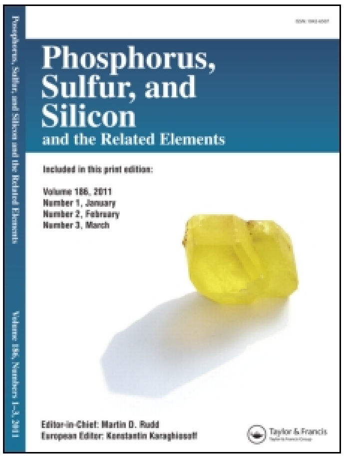

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PHENYLARSENIC(III) DERIVATIVES OF HETEROCYCLIC DITHIOCARBAMATES; SYNTHESIS AND CHARACTERIZATION

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PHENYLARSENIC(III) DERIVATIVES OF HETEROCYCLIC DITHIOCARBAMATES; SYNTHESIS AND CHARACTERIZATION

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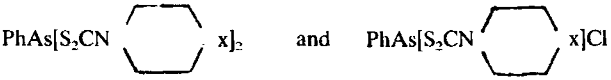
Some new organometallic compounds of arsenic(III) of the type



$PhAs[S_2CN\overline{CH_2CH_2XCH_2CH_2}]_2$ and $PhAs[S_2CN\overline{CH_2CH_2XCH_2CH_2}]Cl$

(where X = >CH_2, >$CH{-}CH_3$, >NH, >$N{-}CH_3$ and >O) have been synthesized by the reactions of $PhAsCl_2$ with sodium salt of substituted heterocyclic dithiocarbamates in 1:2 and 1:1 molar ratios in benzene solution. These complexes have been characterized on the basis of elemental analysis, molecular weight measurements and spectral (IR, ^1H and ^{13}C NMR) studies.

Key words: Phenylarsenic, dithiocarbamates, NMR, IR spectra.

INTRODUCTION

Organoarsenic(III) compounds are known to be biologically active and find applications in various fields.[1-3]

The organic derivatives of phenylarsenic(III) with chelating ligands are of special interest as in these compounds the metal atom may have the coordination number three, four or five depending upon the number of chlorine groups replaced and behavior of the ligand moiety. In this work the synthesis and characterization of some heterocyclic dithiocarbamate complexes of phenylarsenic(III) is reported.

RESULTS AND DISCUSSION

The interaction of phenylarsenic(III) dichloride with sodium salts of heterocyclic dithiocarbamate in benzene solution in 1:2 and 1:1 molar ratios, respectively leads to the formation of the corresponding phenylarsenic(III) derivatives.

$$PhAsCl_2 + n\overline{CH_2CH_2XCH_2CH_2N}CS_2Na \longrightarrow PhAs[S_2C\overline{NCH_2CH_2XCH_2CH_2}]_nCl_{2-n} + nNaCl\downarrow$$

where, X = >CH_2(Pipdtc), >$CH{-}CH_3$(4-MePipdtc), >NH($P_z$dtc), >$N{-}CH_3$(N-Me$P_z$dtc) and >O (Morphdtc); n = 2, 1.

Precipitated sodium chloride was filtered off and the solvent removed under reduced pressure to yield white to pale yellow crystalline solids with sharp melting points. These crystalline solids are soluble in common organic solvents except the bis- and chloro-derivatives of piperazinedithiocarbamates. These derivatives have been purified by recrystallization from chloroform and n-hexane mixture. Osmometric molecular weight measurements at 45°C reveal their monomeric nature in chloroform solution (Table III).

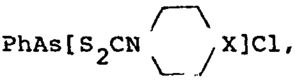
IR Spectra

Infrared spectra of these derivatives have been recorded in the range 4000–400 cm^{-1} as KBr pellets.

The analysis of the $\nu(C \overset{\dots}{-} S)$ absorption band observed at ~1000 cm^{-1} provide useful informations regarding the bonding mode of the ligands. The bands present in the 1000 ± 20 cm^{-1} range show one intense absorption band at ~980 cm^{-1} and a weak shoulder at ~1010 cm^{-1}. This indicates that the ligand acts as a monodentate.[4–7] The monodentate nature of the ligands in these complexes have been further confirmed by the appearance of a downward shift in the position of $\nu(C \overset{\dots}{-} N)$ mode which was observed in the range 1440 ± 15 cm^{-1}.[8]

The bonding of the sulfur atom with the central arsenic atom is confirmed by the appearance of the band ν(As—S)[9] in the range 400–390 cm^{-1}. The band observed in the region 468–460 cm^{-1} has been assigned to the ν(As—C)[10] mode.

In the spectra of the chloro derivatives



similar bands are observed and a new band appears in the region 356–348 cm^{-1} which has been assigned to the ν(As—Cl)[11] mode.

NMR Spectra

The ^{1}H NMR spectra of these complexes has been recorded in $CDCl_3$ solution and the observed chemical shift data are being summarized in Table I.

The characteristic proton resonances due to methyl, ring—CH_2, >N—CH_3, >CH—CH_3 and $(CH_2)_2O$ have been observed at their appropriate positions and do not show any appreciable shift in their position compared to the spectra of the corresponding ligand. The aromatic protons appear in the region δ 6.40–8.50 as a multiplet.

The ^{13}C NMR spectra of these complexes were recorded in chloroform solution and are summarized in Table II. A comparative study of ^{13}C NMR spectra of phenylarsenic(III) complexes with those of the sodium salt of heterocyclic dithiocarbamates[12] shows a remarkable upfield shift in the signal for CS_2 carbon atom. This shift may be due to the bidentate behavior of the dithiocarbamate moiety.

TABLE I

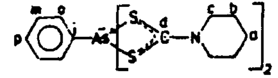
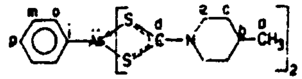
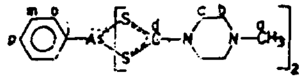
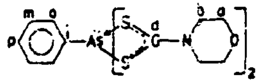
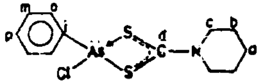
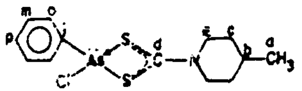
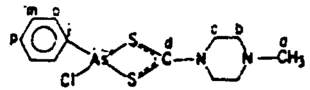
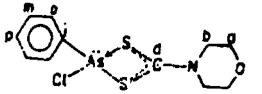
^1H NMR spectral data of heterocyclic dithiocarbamates derivatives of phenylarsenic(III). (δ) ppm (Value indicated in the table represents the protons in the bold letters)

Complex	$-CH_3$	$CH_2<^{CH_2-}_{CH_2-}$	Me->CH	$Me-C<^{CH_2-}_{CH_2-}$	$Me-N<^{CH_2-}_{CH_2-}$	$>C-N<^{CH_2-}_{CH_2-}$	$O<^{CH_2-}_{CH_2-}$	$As-C_6H_5$
$PhAs[Pipdtc]_2$	-	1.56 (6H)	-	-	-	3.97(s) (4H)	-	7.28-8.04(m) (5H)
$PhAs[4\text{-}MePipdtc]_2$	0.98(d) (3H)	-	1.20-1.77(m) (1H)	3.13(t) (4H)	-	5.02(d) (4H)	-	7.32-8.11(m) (5H)
$PhAs[N\text{-}MePzdtc]_2$	2.41(s) (3H)	-	-	-	2.49(d) (4H)	3.81(s) (4H)	-	7.31-8.12(m) (5H)
$PhAs[Morphdtc]_2$	-	-	-	-	-	3.84(s) (4H)	4.11 (4H)	7.42-8.13(m) (5H)
PhAs[Pipdtc]Cl	-	1.53 (6H)	-	-	-	3.71(d) (4H)	-	7.36-7.93(m) (5H)
PhAs[4-MePipdtc]Cl	0.31(d) (3H)	-	4.15 (1H)	2.01 (4H)	2.01 (4H)	-	-	7.64-8.40(m) (5H)
PhAs[N-MePzdtc]Cl	2.28 (3H)	-	-	-	2.45 (4H)	4.11 (4H)	-	7.28-7.95(m) (5H)
PhAs[Morphdtc]Cl	-	-	-	-	-	3.66 (4H)	3.86 (4H)	7.42-8.09(m) (5H)

$PhAs[S_2C\overline{NCH_2CH_2XCH_2CH_2}]_nCl_{2-n}$ where X = $>CH_2$(Pipdtc), $>CH-CH_3$(4-MePipdtc), $>NCH_3$(N-MePzdtc), $>O$(Morphdtc), respectively.

TABLE II

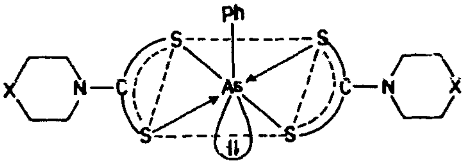
^{13}C NMR spectral data of heterocyclic dithiocarbamate derivatives of phenylarsenic(III) (δ) ppm

Complex	C^a	C^b	C^c	C^d	C^e	$As-C_6H_5$*	δ'	σR°
	23.56	25.46	51.79	194.81	-	133.16 128.06 132.39 127.58	-4.81	-0.21
	21.02	30.12	33.48	194.92	51.03	144.51 128.06 133.21 127.58	-5.63	-0.25
	50.16	54.01	57.86	196.32	-	144.15 128.61 133.27 127.67	-5.60	-0.25
	50.00	65.76	-	195.60	-	144.86 129.26 132.62 128.12	-4.50	-0.20
	22.75	25.24	50.97	191.29	-	145.67 129.53 130.99 128.23	-2.76	-0.12
	18.25	45.34	50.05	196.27	53.95	149.41 130.32 131.21 128.39	-2.82	-0.12
	22.70	25.24	50.92	191.02	-	145.62 129.53 130.94 128.23	-2.71	-0.12
	49.46	65.55	-	193.94	-	145.48 129.91 131.26 128.39	-2.87	-0.13

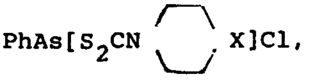
* Metal phenyl values are given in the order C(i), C(o), C(m) and C(p), respectively.

The 'corrected chemical shift' value $\delta'^{13,14}$ defined as $\delta' = \delta C_p - \delta C_m$ (where δC_p and δC_m are the chemical shift values of para and meta carbon atom of the phenyl ring, respectively) and the $\sigma R°$ (Hammett Traft's constant)[15] are found to be in range $\delta -4.50$ to -5.63 and $\delta -0.25$ to -0.20, respectively for these phenylarsenic derivatives. These negative values indicate an electron release from the arsenic atom to phenyl ring through $d\pi - p\pi$ conjugation and poor donor capability of the arsenic atom.

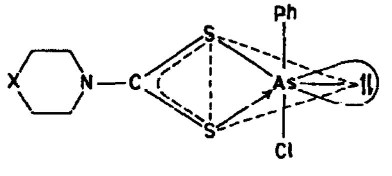
Although the IR spectral data of these complexes in the solid state indicate the monodentate nature of the ligand moieties, in the ^{13}C NMR spectra a significant shift in the position of CS_2 carbon signal reveals the bidentate nature of the ligand moieties, supporting a five coordination around the central arsenic atom with the following pseudo-octahedral geometry.

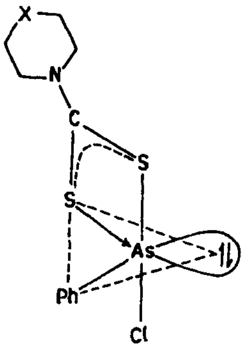


In the spectra of the chloro derivatives,



a similar shift was observed in the position of the CS_2 carbon signal as compared with the spectra of the corresponding sodium salt of ligands, this confirms the bonding of the ligand moiety with phenylarsenic(III) through the S,S atoms. Two sets of phenyl carbon signals are observed in the spectra of chloro derivatives. This may be due to the existence of chloro derivatives in two geometrical isomeric forms in approximately equal ratio:





where X = $\rangle CH_2$(Pipdtc), $\rangle CH—CH_3$(4-MePipdtc), $\rangle NH(P_zdtc)$, $\rangle N—CH_3(N-MeP_zdtc)$ and $\rangle O$ (Morphdtc).

TABLE III

Synthetic and analytical data of phenylarsenic(III) complexes of heterocyclic-dithiocarbamates

Reactants gm		Molecular formula (% yield)	M.P. (±1°C)	NaCl(gm) Found (Calc.)	Analysis			Mol.wt. Found (Calc.)
$NaS_2C\overline{NCH_2CH_2XCH_2CH_2}$	$PhAsCl_2$				As% Found (Calc.)	S% Found (Calc.)	Cl% Found (Calc.)	
X = $>CH_2$								
1.67	0.85	$C_{18}H_{25}N_2S_4As$ (78)	178	0.43 (0.44)	15.80 (15.85)	27.01 (27.13)	-	467 (472.57)
X = $>CH-CH_3$								
1.54	0.79	$C_{20}H_{29}N_2S_4As$ (90)	156	0.40 (0.41)	14.65 (14.96)	25.43 (25.61)	-	498 (500.62)
X = $>NH$								
1.72	0.80	$C_{16}H_{23}N_4S_4As$ (86)	330	0.41 (0.42)	15.49 (15.78)	26.80 (27.82)	-	-
X = $>NCH_3$								
2.34	1.11	$C_{18}H_{27}N_4S_4As$ (80)	358	0.55 (0.58)	14.81 (14.90)	25.46 (25.51)	-	496 (502.60)
X = $>O$								
2.23	1.12	$C_{16}H_{21}N_2S_4O_2As$ (86)	182	0.56 (0.59)	15.53 (15.72)	26.75 (26.90)	-	476 (476.51)
X = $>CH_2$								
2.50	2.54	$C_{12}H_{15}NS_2ClAs$ (80)	86	0.64 (0.66)	21.32 (21.54)	18.01 (18.43)	10.01 (10.19)	344 (347.75)
X = $>CH-CH_3$								
1.08	1.12	$C_{13}H_{17}NS_2ClAs$ (86)	130	0.26 (0.29)	20.34 (20.76)	17.40 (17.77)	9.55 (9.82)	356 (360.77)
X = $>NH$								
1.25	1.17	$C_{11}H_{14}N_2S_2ClAs$ (90)	232	0.29 (0.31)	21.20 (21.47)	18.02 (18.37)	9.98 (10.16)	-
X = $>NCH_3$								
3.22	3.07	$C_{12}H_{16}N_2S_2ClAs$ (86)	80	0.77 (0.79)	20.40 (20.64)	17.50 (17.66)	9.62 (9.76)	360 (362.76)
X = $>O$								
1.05	1.11	$C_{11}H_{13}NS_2OClAs$ (95)	136	0.27 (0.29)	21.23 (21.41)	18.12 (18.33)	10.00 (10.13)	342 (349.72)

The presence of these two geometrical forms could not be detected by ^{1}H NMR spectra.

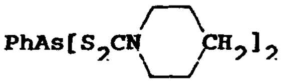
However the possibility of the existence of these ligands as monodentate moieties in the solid state cannot be ruled out. This has been indicated by the IR spectra (which were taken in the solid state). This has also been observed in the diorganoantimony analogues of these dithiocarbamate moieties.[12]

The appearance of negative values for δ'(δ − 2.87 to − 2.71) and σR° (δ − 0.12 to − 0.26) in these chloro derivatives indicate the similar trend in electron release and donor capability of arsenic as described earlier in the case of the bis-derivatives.

EXPERIMENTAL

All the reactions were carried out under anhydrous conditions. The chemicals used were of reagent grade. Phenylarsenic(III) dichloride[16] and heterocyclic dithiocarbamate[17] were prepared by literature methods. Arsenic, sulfur and chlorine were estimated by iodometric, gravimetric and Volhard's methods respectively.[18] Molecular weights were determined on Knauer vapour pressure osmometer in chloroform solution at 45°C. IR spectra were recorded on Nicolet Dx-FT-IR spectrometer using as KBr pellets. NMR spectra (^{1}H and ^{13}C) of these complexes and sodium salt of ligands were recorded on JEOL-FX-90Q (90 MHz) spectrometer in $CDCl_3$/DMSO-d_6 and $CHCl_3$/DMSO solutions, respectively, using TMS as an internal reference.

All the complexes have been synthesized by a similar route and therefore for brevity the synthetic procedure for a representative complex is being described below and the analytical details of the other complexes are summarized in Table III.

Synthesis of 

A benzene solution of $PhAsCl_2$ (0.85 g, 3.81 mM) was added dropwise with constant stirring of the benzene suspension of the sodium salt of piperidine dithiocarbamate (1.67 g, 7.61 mM). The reaction mixture was refluxed for ~4 hours. Sodium chloride thus formed was filtered off and the excess solvent from the filtrate was removed under reduced pressure. The resultant off-white solid was recrystallized from chloroform/pet.ether mixture and dried under vacuum (yield, 78%). As = 15.80 and S = 27.01%; calculated for $C_{18}H_{25}N_2S_4As$; As = 15.85 and S = 27.12%.

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