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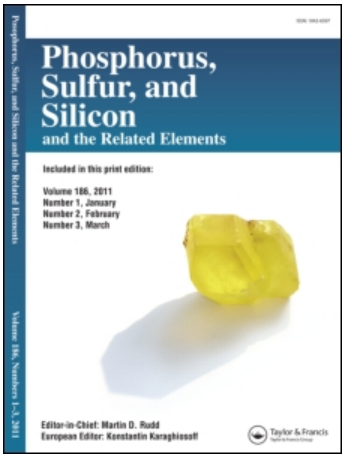

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H. P. S. Chauhan; S. Chourasia; B. Nahar; R. K. Singh

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SYNTHESIS AND CHARACTERISATION OF MIXED DITHIOLATOARSENIC(III) ALKYLDITHIOCARBONATES AND DIALKYLDITHIOCARBAMATES

H.P.S. CHAUHAN*, S. CHOURASIA, B. NAHAR and R.K. SINGH

Institute of Chemical Sciences, Devi Ahilya University, Takshashila Campus, Khandwa Road, Indore-452001, India

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Mixed dithiolatoarsenic (III) alkyldithiocarbonate and dialkyldithiocarbamate derivatives of the type $\overline{SCH_2CH_2SAs}(S_2COR)$, [where R = Et, Pr^n, Pr^i, Bu^n & Bu^i] and $\overline{SCH_2CH_2SAs}(S_2CX)$, [where X = NMe_2, NEt_2 and $N(CH_2CH_2)_2$] are reported. These are synthesised by the simple replacement reactions of 2-chloro-1,3-dithia-2-arsacyclopentane with potassium alkylxanthate and with sodium dialkyldithiocarbamate in 1:1 molar ratios in benzene respectively. These derivatives have been characterised by elemental analyses, melting point determinations as well as IR & NMR (^1H and ^{13}C) spectral studies and tentative structures have been proposed.

Keywords: Dithiolatoarsenic; dithiocarbamates; dithiocarbonates; IR spectra; NMR spectra

INTRODUCTION

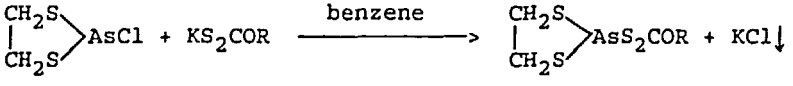
Although several xanthates[1–3] mixed halide xanthates[4] and tris[5–7] as well as organometallic dithiocarbamates[8] of arsenic have been known and some of them are fully characterised by X-ray crystal structure[8–12], the corresponding mixed dithiolatoarsenic complexes do not appear to have received much attention. More recently, the structures of $(CH_2S)_2AsS_2CN(CH_2CH_2)_2O$[13], $(CH_2S)_2AsS_2CN[(CH_2)_3C(O)]$[13]and $O(C_6H_4)_2AsS_2CN(CH_2CH_2)_2$14 have been reported. Our interest in the

* Author to whom correspondence to be addressed.

group 15 metal derivatives of dithiolato ligands[15–18] has prompted us to investigate the alkyldithiocarbonates and dialkyldithiocarbamates of arsenic(III).

RESULTS AND DISCUSSION

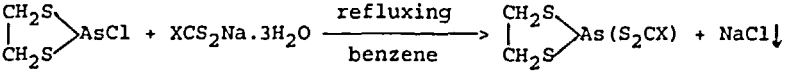
2-chloro-1,3-dithia-2-arsacyclopentane reacts with potassium alkylxanthates in 1:1 molar ratio in benzene at room temperature to give mixed dithiolatoarsenic(III) alkyldithiocarbonates.



where R = Et, Pr^n, Pr^i, Bu^n and Bu^i.

All these compounds are stable yellow viscous liquids at room temperature except the isopropyl dithiocarbonate derivative which is a yellow solid. These are soluble in $CDCl_3$, benzene, CS_2 etc.

Mixed dithiolatoarsenic(III) dialkyldithiocarbamates are synthesised by reacting 2-chloro-1,3-dithia-2-arsacyclopentane with sodium diethyldithiocarbamate in 1:1 molar ratios in refluxing benzene.



where X = NMe_2, NEt_2 and $N(CH_2CH_2)_2$.

These are low melting, yellow crystalline solids, soluble in $CDCl_3$, benzene, CCl_4etc.

Infra-red Spectra

IR spectra of these compounds have been recorded in the range 4000–200 cm^{-1} and the characteristic bands have been assigned on the basis of earlier published work[14,19–22].

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The bands of medium to strong intensity observed in the region 1412–1480 cm^{-1} may be attributed to C⁼⁼⁼N stretching vibrations of dithiocarbamate moieties. In the spectra of dithiocarbonate derivatives, very strong bands observed in region 1225–1240 cm^{-1} and medium to weak intensity bands observed in the region 1150–1160 cm^{-1} have been assigned to ν(C-O-C) and ν(C-O) vibrations, respectively. All these complexes show medium to strong absorption bands in the region 985–1060 cm^{-1} for C⁼⁼⁼S stretching vibrations and medium absorption bands in the region 325–400 cm^{-1} for ν(As—S) vibrations. The appearance of a single strong band for ν(C⁼⁼⁼N) and for ν(C⁼⁼⁼S) vibrations reflects the bidentate nature of the dithiocarbamate[14,19] and dithiocarbonate[20] moieties in these complexes.

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^{1}HNMR Spectra

The ^{1}HNMR spectra of these derivatives have been recorded in $CDCl_3$ solutions using TMS as internal standard. The spectra of these complexes exhibit the expected pattern[4,10,14,15]without any appreciable shifts.

A sharp singlet due to CH_2S protons of both dithiocarbamate and dithiocarbonate derivatives have been observed in the region 3.55–3.59 δppm indicating that these protons are magnetically equivalent. In addition, these compounds also show expected proton resonances due to corresponding N-alkyl and alkoxy protons of dithiocarbamate and dithiocarbonate moieties, respectively (Table-I). No remarkable change has been observed other than some broadening in the signals of N-alkyl protons of dialkyldithio-carbamate[21,22].

^{13}CNMR Spectra

^{13}CNMR spectra of a few alkyldithiocarbonate complexes and only one representative dialkyldithiocarbamate complex have been recorded using TMS as internal standard. The ^{13}CNMR signals thus obtained are at reported values[10,14,21] without any appreciable shifts. The ^{13}CNMR spectral data of all the alkyldithiocarbonate and dialkyldithiocarbamate derivatives (Table-I) exhibit a signal at 41–43 δppm due to dithia

arsacyclopentane (CH_2S) carbons indicating that these two carbon atoms are magnetically equivalent thus supporting the results of ^{1}HNMR spectra. The alkyldithiocarbonate derivatives and dimethyldithiocarbamate derivative also show a signal at ~216 δppm and ~195 δppm due to OCS_2 and NCS_2 carbon atoms, respectively. In addition, these complexes also exhibit the expected signals due to corresponding alkoxy and N-alkyl carbon atoms.

On the basis of the above spectral data it may be concluded tentatively that the ligands behave as bidentate moieties[14,19,20] in both the type of complexes, thus leading to distorted trigonal bipyramidal or distorted tetragonal pyramidal geometry, with a stereochemically active lone pair occupying one of the positions.

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EXPERIMENTAL

Owing to the hydrolysable nature of dithiocarbonate and dithiocarbamate ligands, all the experiments were carried out in moisture free conditions. Solvents like benzene, ethanol, n-propanol, i-propanol, n-butanol and i-butanol were dried by standard methods[24]. Potassium alkyl xanthates[25] and 2-chloro-1,3-dithia-2-arsacyclopentane were prepared by earlier reported methods. Sodium and ammonium dialkyldithiocarbamates (Fluka) were used as received. Arsenic was estimated iodometrically[26] and sulfur gravimetrically as $BaSO_4$.

(a)Reaction of 2-chloro-1,3-dithia-2-arsacyclopentane with potassium isopropylxanthate in 1:1 molar ratio in benzene

A solution of 2-chloro-1,3-dithia-2-arsacyclopentane (1.25 g; 6.16 mmol) in benzene (40 ml) was taken in a round bottom flask and potassium isopropylxanthate (1.07 g; 6.15 mmol) was added to it. The reaction mixture was stirred for ~4 hours. Precipitated potassium chloride (0.40 g) was removed by filtration. The filtrate was reduced under reduced pressure to give yellow crystals which were dried and weighed. (M.P. = 64°C; yield = 1.75 g; 94%).

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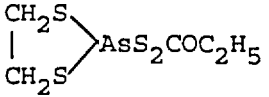
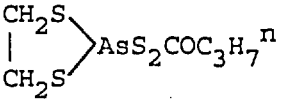
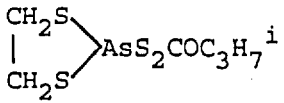
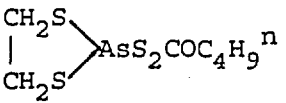
TABLE I ^{1}H & $^{13}CNMR$ spectral data of dithiolate alkyldithiocarbonate and dialkyldithiocarbamate derivatives of arsenic(III)

S. No.	*Compounds*	*$^{1}HNMR$ chemical shift (δppm)*	*$^{13}CNMR$ chemical shift (δppm)*
1.		1.43, t, 3H (CH_3) ; J(OCH_2-CH_3) = 7.2 Hz 3.57, s, 4H(CH_2S) 4.63, q, 2H(OCH_2) ; J(CH_3-CH_2O) = 7.2 Hz	14.0 (CH_3) 43.0 (CH_2S) 71.0 (OCH_2) 217.0 (OCS_2)
2.		1.02, t, 3H(CH_3) ; J(CH_2-CH_3) = 8.5 Hz 1.74–1.95, sex 2H(CH_2) , J(CH_3-CH_2) = 8.5 Hz 3.59, s, 4H(CH_2S) 4.53, t, 2H(OCH_2) ; J(CH_2-CH_2O) = 8.5 Hz	
3.		1.35, d, 6H(CH_3) ; J(OCH-CH_3) = 6 Hz 3.50, s, 4H(CH_2S) 5.50–5.57, h, 1H(OCH); J(CH_3-CHO) = 6 Hz	21.0 (CH_3) 43.0 (CH_2S) 79.0 (OCH) 216.0 (OCS_2)
4.		0.92, t, 3H(CH_3) ; J(CH_2-CH_3) = 8 Hz 1.39–1.57, sex, 2H(CH_2) , J(CH_3-CH_2) = 8 Hz 1.72–1.86, qu, 2H(CH_2) , J(CH_2CH_2) = 8 Hz 3.57, s, 4H(CH_2S) 4.55, t, 2H(OCH_2) ; J(CH_2-CH_2O) = 8 Hz	14.0 (CH_3) 19.0 (CH_2) 30.0 (CH_2) 43.0 (CH_2S) 74.0 (OCH_2) 216.5 (OCS_2)

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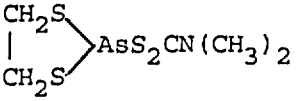
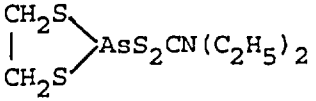
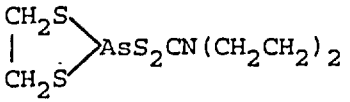
S. No.	*Compounds*	*^{1}HNMR chemical shift (δppm)*	*^{13}CNMR chemical shift (δppm)*
5.		3.40, bs, 6H(CH_3N) 3.56, s, 4H(CH_2S)	41.0 (CH_2S) 42.0 (CH_3) 195.0 (NCS_2)
6.		1.28, t, 6H(CH_3) ; J(CH_2-CH_3) = 7.5 Hz 3.55, s, 4H(CH_2S) 3.82, bq, 4H(CH_2N)	
7.		1.92–2.15, m, 4H(CH_2CH_2N) 3.55, s, 4H (CH_2S) 3.60–3.85, bm, 4H(CH_2N)	

s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet,
sex = sextet, h = septet, m = multiplet & b = broad.

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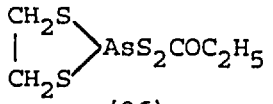
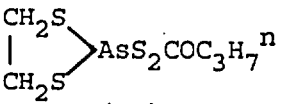
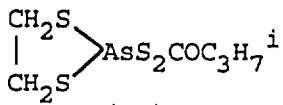
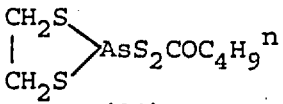
TABLE II Analytical data for alkyldithiocarbonate and dialkyldithiocarbamate derivatives of arsenic(III)

S. No.	Compounds (yield %)	Physical state M.P. (°C)	NaCl/KCl Found (Calcd) g	Analysis of % Found (Calcd)				
				As	S	C	H	N
1.	 (96)	Yellow viscous liquid	0.35 (0.36)	25.72 (26.00)	43.80 (44.42)	19.98 (20.82)	3.00 (3.12)	---
2.	 (92)	Yellow viscous liquid	0.34 (0.37)	24.41 (24.73)	41.86 (42.36)	23.46 (23.83)	3.70 (3.64)	---
3.	 (94)	Yellow solid (64)	0.40 (0.45)	25.27 (24.73)	42.01 (42.36)	23.67 (23.83)	3.75 (3.64)	---
4.	 (90)	Yellow viscous liquid	0.37 (0.37)	22.98 (23.69)	40.64 (40.49)	26.10 (26.57)	3.89 (4.11)	---

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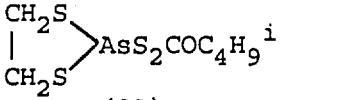
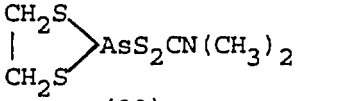
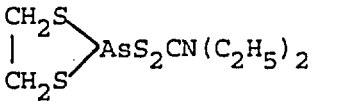
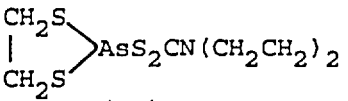
S. No.	Compounds (yield %)	Physical state M.P. (°C)	NaCl/KCl Found (Calcd) g	Analysis of % Found (Calcd)				
				As	*S*	*C*	*H*	*N*
5.	 (98)	Yellow viscous liquid	0.38 (0.40)	24.10 (23.69)	40.96 (40.49)	26.35 (26.57)	4.00 (4.11)	---
6.	 (98)	Off white solid (84)	0.28 (0.23)	26.51 (26.11)	44.08 (44.61)	20.80 (20.91)	3.47 (3.48)	4.28 (4.87)
7.	 (90)	White solid (97)	0.49 (0.40)	24.07 (23.79)	39.95 (40.64)	26.59 (26.67)	4.32 (4.44)	4.34 (4.44)
8.	 (89)	White solid (130)	0.52 (0.49)	23.98 (23.94)	39.98 (40.90)	26.70 (26.84)	3.80 (3.83)	4.50 (4.47)

(b)Reaction of 2-chloro-1,3-dithia-2-arsacyclopentane with sodium dimethyl dithiocarbamate in 1:1 molar ratio in benzene

A solution of 2-chloro-1,3-dithia-2-arsacyclopentane (0.81 g; 4.00 mmol) in benzene (40 ml) and sodium dimethyl dithiocarbamate (0.72 g; 4.01 mmol) was refluxed for ~5 hrs. Precipitated sodium chloride (0.28 g) was separated by filtration. Solvent was reduced from filtrate to give white crystals.
(M.P. = 84°C; yield = 1.13 g; 98%).

Other derivatives listed in Table-2 were synthesised by adopting either of the above routes a and b.

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