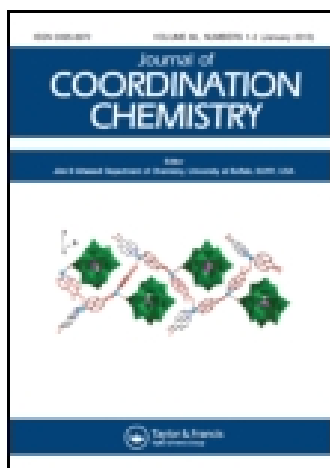


This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:39
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Coordination chemistry of trivalent and pentavalent organoarsenic heterocyclic dithiocarbamate derivatives: synthesis and characterization

Deepak Kumar Sharma^a, Rita Gupta^a, Yashpal Singh^a & Jyoti Sharma^a

^a Department of Chemistry, University of Rajasthan, Jaipur, India
Accepted author version posted online: 22 Apr 2014. Published online: 05 Jun 2014.



[Click for updates](#)

To cite this article: Deepak Kumar Sharma, Rita Gupta, Yashpal Singh & Jyoti Sharma (2014) Coordination chemistry of trivalent and pentavalent organoarsenic heterocyclic dithiocarbamate derivatives: synthesis and characterization, *Journal of Coordination Chemistry*, 67:8, 1478-1490, DOI: [10.1080/00958972.2014.916794](https://doi.org/10.1080/00958972.2014.916794)

To link to this article: <http://dx.doi.org/10.1080/00958972.2014.916794>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

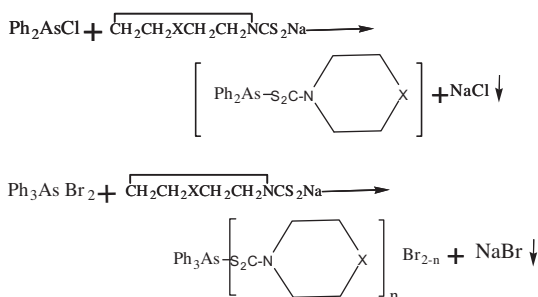
Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Coordination chemistry of trivalent and pentavalent organoarsenic heterocyclic dithiocarbamate derivatives: synthesis and characterization

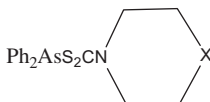
DEEPAK KUMAR SHARMA, RITA GUPTA, YASHPAL SINGH and JYOTI SHARMA*

Department of Chemistry, University of Rajasthan, Jaipur, India

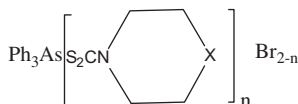
(Received 14 October 2013; accepted 25 March 2014)



A series of diphenylarsenic(III) and triphenylarsenic(V) derivatives of heterocyclic dithiocarbamates of the type:



and



[where X = >CH₂ (Pipdte), >CH-CH₃ (4-MePipdte), >O (Morphdte), >N-CH₃ (N-MePzdtc), and >NH (Pzdtc)] [*n* = 1 or 2] have been synthesized by reactions of diphenylarsenic(III) chloride and triphenylarsenic(V) dibromide with the sodium salt of heterocyclic dithiocarbamates in 1 : 1 and 1 : 2 M ratios, respectively, in refluxing benzene. All these newly synthesized compounds have been characterized by their elemental analyses, molecular weight measurements, and ESI mass studies. Structures of the compounds have been proposed on the basis of IR, ¹H, and ¹³C NMR spectral data which suggest anisobidentate mode of bonding.

*Corresponding author. Email: chem.uor@gmail.com

Keywords: Trivalent; Pentavalent; Organoarsenic; Elemental analyses; NMR spectral data

Introduction

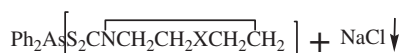
The chemistry of organoarsenic in +3 and +5 oxidation states has been the subject of considerable research [1–4] due to their extensive applications such as fungicides, herbicides, and wood preservatives [5–9]. Organoarsenic(III) and (V) derivatives exhibit different coordination patterns with ligands such as xanthates [10], dithiophosphates [11], dithiocarbamates [12], etc.

Dithiocarbamates are well known as heavy metal chelating agents [13] and have been used in complexes with anti-fouling, anti-scaling, and corrosion inhibiting properties for use in recirculating water coolers [14].

We have been working on organic derivatives of organoarsenic, organoantimony, and organobismuth in +3 and +5 states with some N and S containing ligands [15–20]. In continuation of our work on monophenyl antimony(III) [21] and triphenyl antimony(V) derivatives [22] of heterocyclic dithiocarbamates, in this article we report the synthesis, characterization, and structural elucidation of diphenylarsenic(III) and triphenylarsenic(V) derivatives of heterocyclic dithiocarbamates.

Results and discussion

Diphenylarsenic(III) derivatives of heterocyclic dithiocarbamates have been synthesized by reactions of Ph_2AsCl with the sodium salt of heterocyclic dithiocarbamates in anhydrous benzene with vigorous stirring.



Similarly, triphenylarsenic(V) bromo- and bis(heterocyclic-dithiocarbamate) derivatives have been prepared by the reactions of Ph_3AsBr_2 with the sodium salt of heterocyclic dithiocarbamates in 1 : 1 and 1 : 2 M ratio, respectively, in anhydrous benzene solution with vigorous stirring.



[where $X = >\text{CH}_2$ (Pipdtc), $\text{CH}_3\text{-CH}<$ (4-MePipdtc), $>\text{N-CH}_3$ (N-MePzdtc), $>\text{NH}$ (Pzdtc), and $>\text{O}$ (Morphdtc)] [$n = 1$ or 2].

All these derivatives are colored crystalline solids, soluble in common organic solvents, and recrystallized from benzene and n-hexane mixture.

IR spectra

IR spectra of these derivatives have been recorded as KBr pellets from 4000 to 400 cm^{-1} and the assignment of important bands have been made with the help of earlier reported literature. All the diphenylarsenic(III) and triphenylarsenic(V) derivatives exhibit strong bands at 1430–1445 cm^{-1} , due to $\nu(\text{C-N})$ stretching vibrations. A comparison with the corresponding sodium salt of dithiocarbamates shows a small shift towards higher frequencies ($\sim 20\text{--}35 \text{ cm}^{-1}$). Split strong bands at $\sim 1115\text{--}970 \text{ cm}^{-1}$ and $\sim 1130\text{--}995 \text{ cm}^{-1}$ due to $\nu(\text{C=S})$ have been observed for diphenylarsenic(III) and triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamate) derivatives, respectively.

The coordination pattern of these diphenylarsenic(III) and triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamate) derivatives may be determined by using the value of $\Delta\nu[\nu(\text{CS}_2)_{\text{assy}} - \nu(\text{CS}_2)_{\text{symm}}]$. The values of $\nu(\text{CS}_2)_{\text{assy}}$ and $\nu(\text{CS}_2)_{\text{symm}}$ are at 1110–1120 cm^{-1} and 980–995 cm^{-1} , respectively, for diphenylarsenic(III) derivatives whereas in triphenylarsenic(V) derivatives these stretches are observed at 1115–1125 cm^{-1} and 990–1010 cm^{-1} , respectively. The $\Delta\nu$ value [$\nu(\text{CS}_2)_{\text{assy}} - \nu(\text{CS}_2)_{\text{symm}}$] are 115–130 cm^{-1} and 125–135 cm^{-1} for diphenylarsenic(III) and triphenylarsenic(V) bromo- and bis heterocyclic dithiocarbamate derivatives, respectively, which are smaller than the observed $\Delta\nu$ values for bidentate coordination and are larger than the observed value for corresponding free sodium salt of dithiocarbamates, as reported earlier [23]. The above-mentioned data suggest that the dithiocarbamates are coordinated to arsenic in anisobidentate manner. A sharp absorption band at $450 \pm 20 \text{ cm}^{-1}$ may be assigned to $\nu(\text{As-S})$ which also indicates the bonding of arsenic with sulfur. A band due to $\nu(\text{As-C})$ is observed at 470–455 cm^{-1} in spectra of all these derivatives.

NMR spectra

^1H NMR spectra. ^1H NMR spectra of these diphenylarsenic(III) and triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamate) derivatives have been recorded in CDCl_3 and DMSO-d_6 and the data are summarized in tables 1 and 2.

The $-\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-$, $\text{N}(\text{CH}_3)-$, $\text{CH}_2\text{-O-CH}_2$, protons in spectra of diphenylarsenic(III) derivatives (1–5) and triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamate) derivatives (6–15) are observed at their appropriate positions (tables 1 and 2). No appreciable shift is observed in their chemical shift positions as compared to the corresponding sodium salt of dithiocarbamates is observed. The signals for aromatic ring protons attached to arsenic appear at δ 7.13–8.28 as a multiplet.

^{13}C NMR spectra. ^{13}C NMR spectra of these derivatives are interpreted and data are summarized in tables 3 and 4.

A comparative study of ^{13}C NMR data of diphenylarsenic(III) (heterocyclic dithiocarbamate) derivatives (1–5) and triphenylarsenic(V) derivatives of bromo- and bis(heterocyclic dithiocarbamate) derivatives (6–15) with their corresponding sodium salt of dithiocarbamates indicates the upfield shift of $\sim 15\text{--}20 \text{ ppm}$ in the position of CS_2 carbon signals, due to strong chelation and anisobidentate behavior of dithiocarbamate. Remaining carbon signals for diphenylarsenic(III) and triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamate) derivatives are at their expected positions (tables 3 and 4).

Table 1. ¹H NMR spectral data (δ) of diphenylarsenic(III) (heterocyclic dithiocarbamates).

Compound							-As-Ph	
[Ph ₂ As(Pipdte)]	-	1.25–1.56 (m)	-	-	-	3.95 (s)	7.29–8.05 (m) (5H)	-
[Ph ₂ As(4-Me-pipdic)]	0.75–0.91 (m)	-	-	2.58–2.94 (4H)	1.45–1.63 (m) (1H)	4.12–4.77 (d) (4H)	7.37–8.22 (m) (5H)	-
[Ph ₂ As(Morphdte)]	-	-	-	-	-	3.73	7.26–8.24 (m)	2.45, 2.78
[Ph ₂ As(NMepzdic)]	1.25 (s)	-	2.89–3.15	-	-	3.48–3.87 (m)	7.32–8.18 (m)	-
[Ph ₂ As(Pzdtc)]	-	-	-	-	-	3.74–4.51	7.75–8.12 (m)	-

Table 2. ^1H NMR spectral data (δ) of triphenylarsenic(V) bromo and bis(heterocyclic dithiocarbamates).

Compound	$-\text{CH}_3$	CH_2	$\text{Me}-\text{N}-\text{CH}_2$	$\text{Me}-\text{C}-\text{CH}_2$	$\text{Me}-\text{CH}$	$\text{C}=\text{N}-\text{CH}_2$	$-\text{As}-\text{Ph}$	$\text{O}-\text{CH}_2$
$[\text{Ph}_3\text{As}(\text{Pipdte})\text{Br}]$	—	1.71–1.78 (m)	—	—	—	4.15 (s)	7.36–8.24 (m) (5H)	—
$[\text{Ph}_3\text{As}(4\text{-Me-pipdte})\text{Br}]$	0.94–0.97 (m)	—	—	3.06–3.10 t (4H)	1.23–1.33 (m) (1H)	4.82–4.88 (d) (4H)	7.34–8.10 (m) (5H)	—
$[\text{Ph}_3\text{As}(\text{Morphdte})\text{Br}]$	—	—	—	—	—	3.76, 3.79	7.41–8.07 (m)	2.46, 2.78
$[\text{Ph}_3\text{As}(\text{N-Me-pzdtc})\text{Br}]$	1.21 (s)	—	3.60–3.68	—	—	3.48–3.87 (m)	7.56–8.18 (m)	—
$[\text{Ph}_3\text{As}(\text{Pzdtc})\text{Br}]$	—	—	—	—	—	3.85–4.30	7.75–8.08 (m)	—
$[\text{Ph}_3\text{As}(\text{Pipdte})_2]$	—	1.76–2.16 (m)	—	—	—	4.77 (s)	7.90–8.28 (m)	—
$[\text{Ph}_3\text{As}(4\text{-Me-pipdte})_2]$	0.85–0.91	—	—	3.49–3.76	1.25	4.17–4.48	7.59–8.10 (m)	—
$[\text{Ph}_3\text{As}(\text{Morphdte})_2]$	—	—	—	—	—	3.68–3.72	7.26–8.20 (m)	3.44, 3.51
$[\text{Ph}_3\text{As}(\text{N-Me-pzdtc})_2]$	1.25–1.78	—	3.60–3.87	—	—	4.12 (s)	7.72–8.23 (m)	—
$[\text{Ph}_3\text{As}(\text{Pzdtc})_2]$	—	—	—	—	—	4.69–5.01	7.59–8.08 (m)	—

Table 3. ^{13}C NMR spectral data (δ) of diphenylarsenic(III)(heterodithiocarbamates) (1–5).

Complex	As-C ₆ H ₅ *										σR^e
	Ca	Cb	Cc	Cd	Ce	C(p)	C(m)	C(o)	C_i	δ'	
	23.05	25.59	51.76	192.57		127.28	129.46	131.33	148.43	-1.67	-0.07
	21.15	34.03	51.10	195.83	53.36	128.28	131.73	134.06	134.02	-3.45	-0.14
		48.52	62.36	193.86		128.10	131.76	134.96	148.67	-3.66	-0.15
		51.17	39.15	192.85	52.07	128.90	131.79	135.17	146.72	-2.89	-0.12
		25.83	39.15	192.88		128.59	131.79	135.17	146.42	-2.89	-0.11

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

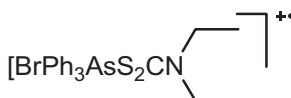
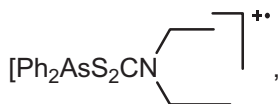
Table 4. ^{13}C NMR spectral data (δ) of new triphenylarsenic(V) bromo and bis(heterodithiocarbamates) (6–15).

Complex	$\text{As-C}_6\text{H}_5^*$										
	Ca	Cb	Cc	Cd	Ce	C(p)	C(m)	C(o)	C(i)	δ	σR^p
	22.40	26.33	52.78	192.65		128.28	129.22	131.33	132.43	-1.04	-0.04
	22.37	44.58	52.77	192.60	55.80	128.28	130.03	131.42	133.70	-1.75	-0.24
		52.04	66.12	193.84		128.10	131.76	133.96	138.67	-4.37	-0.18
		52.53	50.95	193.86		128.59	131.21	134.15	141.01	-3.06	-0.13
		51.17	39.15	193.85	51.37	128.90	131.79	135.17	142.42	-2.89	-0.12
	18.40	54.33	58.34	193.58		128.56	131.21	134.00	138.35	-2.90	-0.14
	21.33	31.18	52.07	192.74	51.20	128.31	131.65	136.17	141.67	-3.34	-0.14
		76.13	66.12	193.83		128.54	130.94	135.03	138.36	-2.25	-0.25
		50.78	45.57	193.59	54.49	128.33	130.79	133.49	138.37	-2.46	-0.27
		52.75	51.99	193.83		128.39	130.83	133.89	138.36	-2.55	-0.11

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

The corrected chemical shift value [24] δ' and Hammett–Taft constant [25] σR° for phenyl carbons attached to arsenic in +3 and +5 oxidation states have been calculated by the relation $\delta' = C_p - C_m$ (where C_p and C_m are the chemical shift values of para and meta carbons of phenyl ring attached to arsenic) and by the equation $\delta' = 23.06 \sigma R^\circ$, respectively. The δ' and σR° values are negative, δ' -3.66 to -1.68 for **1–5** and -4.37 to -1.04 for **6–15** and their σR° values are -0.15 to -0.07 for **1–5** and -0.27 to -0.04 for **6–15**. These negative values exhibit the release of electron density from metal towards the phenyl ring through $d\pi-p\pi$ conjugation in these derivatives and poor donor capability of arsenic.

ESI mass spectra. ESI mass spectral data of three compounds, one each from diphenylarsenic(III) heterocyclic dithiocarbamates (**1**), triphenylarsenic(V) bromo- (**6**) and bis(heterocyclic dithiocarbamates) (**11**) series have been recorded which exhibit monomers of these compounds and their fragmentation patterns are summarized in tables 5–7, respectively, the mass peaks indicated formation of a variety of fragments of arsenic – dithiocarbamate moieties in the course of decomposition. In all three compounds the molecular ion peak appeared but was not the base peak. Base peaks at m/z 379.50, 531.90, and 108.90 correspond to the fragments



and



respectively, indicating strong chelating of dithiocarbamate. Fragmentation of complex initiated from the heterocycle of the dithiocarbamate and sequentially there is partial loss of the dithiocarbamate and completely loss of phenyl, attached to As. We get $\{\text{As-S}\}^+$ fragment as a final decomposition product in each compound, showing strong As–S bonding.

Table 5. ESI-Mass fragmentation mode of **1**.

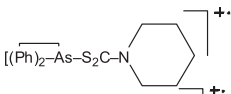
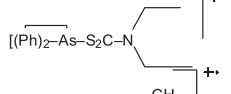
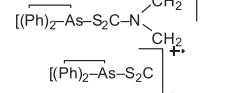
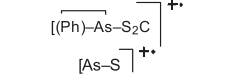


S.no.	Assignment	Mass no.	Relative abundance (%)
1		392.80/389.60	21.77/19.44
2		379.50/376.10	100
3		315.60/316.20	12.05/11.11
4		273.20/274.30	27.77/13.88
5		196.10/197.20	5.55/4.83
6		108.30/106.30	4.61/4.01

Table 6. ESI-mass fragmentation mode of **6**.

S.no.	Assignment	Mass no.	Relative abundance (%)
1		546.40/545.70	33.80/30.98
2		531.90/530.10	100
3		503.20/502.30	20.33/18.30
4		426.30/427.10	64.28/61.29
5		230.80/231.40	15.49/12.67
6		108.30/106.70	21.05/12.67

Table 7. ESI-mass fragmentation mode of **11**.

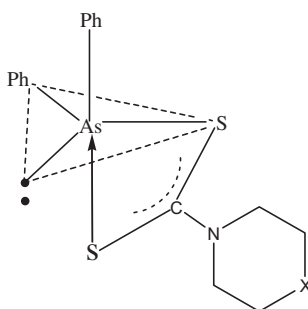
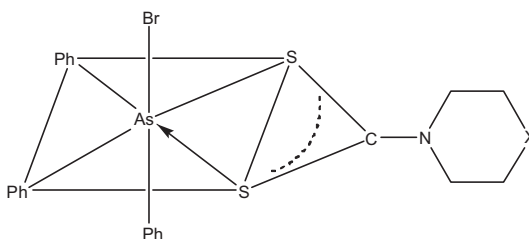
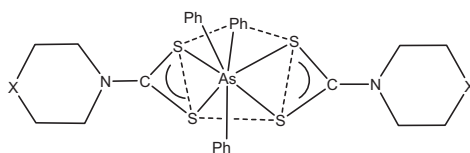
S. no.	Assignment	Mass no.	Relative abundance (%)
1		627.20/626.70	16.92/13.84
2		473.80/472.10	6.15/7.15
3		445.30/447.60	16.92/12.30
4		213.90/215.30	15.30/6.15
5		187.70/186.20	9.23/8.17
6		108.30/106.70	100

In the mass spectrum of triphenyl(V)bromo-(heterocyclic dithiocarbamate), two lines of almost equal height (1 : 1) are observed in the molecular ion region with a gap of 2 m/z unit (i.e. M^+ and $M+2$) between them. This indicates the presence of a bromine in this compound. Compounds containing bromine exhibit two peaks M^+ and $M+2$ (1 : 1) in molecular ion region, depending on which bromine isotope ($^{79}\text{Br}/^{81}\text{Br}$), the molecular ion contains.

Structural elucidation. The molecular structure of these diphenyl arsenic(III) (heterocyclic dithiocarbamates) and triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamates) in the solid state may be assigned on the basis of earlier reported crystallographic structures of similar derivatives [26].

IR spectra displayed a split strong band at $1130\text{--}970\text{ cm}^{-1}$ due to $\nu(\text{C}=\text{S})$. In diphenyl arsenic(III) dithiocarbamate derivatives $\nu(\text{C}=\text{S})$ was at lower wavenumber as compared to triphenylarsenic(V)bromo- and bis(heterocyclic dithiocarbamate).

^{13}C NMR spectral studies exhibit remarkable upfield shifts in the position of CS_2 carbon indicating a strong chelation in all these derivatives. The spectroscopic evidence suggests that the dithiocarbamate moieties are coordinated with arsenic in an anisobidentate manner with arsenic in a trigonal bipyramidal geometry having stereochemically active lone pair

Figure 1. Proposed structure for **1–5**.Figure 2. Proposed structure for **6–10**.Figure 3. Proposed structure for **11–15**.

electrons for diphenyl arsenic(III) derivatives of heterocyclic dithiocarbamate derivatives (**1–5**) (figure 1).

In triphenyl arsenic(V) bromo- (**6–10**) and bis(heterocyclic dithiocarbamate) derivatives (**11–15**) arsenic acquires octahedral and pentagonal bipyramidal geometries (figures 2 and 3), respectively.

Conclusion

A comparative study of triphenylarsenic bromo- and bis(heterocyclic dithiocarbamate) derivatives of heterocyclic dithiocarbamate in +5 oxidation state with diphenyl arsenic derivatives of heterocyclic dithiocarbamate in +3 oxidation state reveals that the coordination pattern of dithiocarbamate in both +5 and +3 oxidation state is the same. Strong electron attraction of arsenic in +5 oxidation is manifested by more downfield shift in the position

of >C-N and CS₂ carbons in ¹³C NMR spectra and similar trend is observed in ¹H NMR spectra of the protons adjacent to C-N carbon.

The δ' and σR° values for triphenylarsenic derivatives in +5 oxidation state are more negative than in diphenyl arsenic derivatives in +3 oxidation state which reveal more electron transfer from central arsenic to the phenyl rings.

Experimental

All preparations and subsequent manipulations were carried out under moisture free conditions and glassware was carefully dried prior to use. Benzene and n-hexane were dried by standard methods.

Diphenylarsenic chloride (Ph₂AsCl) [27], triphenylarsenic dibromide [28] (Ph₃AsBr₂), and sodium salts of heterocyclic dithiocarbamate [29] have been synthesized by literature methods. Arsenic and sulfur were estimated by iodometric and gravimetric methods [30], respectively.

IR spectra of these compounds have been recorded as Nujol mulls using KBr pellets from 4000 to 400 cm⁻¹ on a FT-IR Spectrophotometer model 8400S Shimadzu. The ¹H and ¹³C NMR spectra have been recorded on a JEOL-FTAL 300 MHz spectrometer in CDCl₃/DMSO-d₆ solutions using TMS as an internal reference.

Synthesis of diphenylarsenic(III)-(piperidine-dithiocarbamate) derivative

The reaction mixture containing equimolar amount of sodium salt of pipdte (0.92 g, 5.01 mM) and Ph₂AsCl (1.36 g, 5.04 mM) in benzene (50 mL) was stirred for ~6 h at room temperature (~25 °C). The NaCl thus formed was filtered off and excess solvent was removed from the filtrate under reduced pressure to produce the compound as a brownish solid in quantitative yield. The product was recrystallized from benzene and n-hexane mixture.

Analysis showed As% (19.51), S% (17.01), C% (54.82), H% (5.14), N% (3.57) calculated for C₁₈H₂₀AsNS₂ As% (18.99), S% (16.25), C% (54.80), H% (5.10), N% (3.54). The other compounds were synthesized by similar methods. The synthetic and analytical data are summarized in table 8.

Table 8. Synthetic and analytical data of diphenylarsenic(III) (heterocyclic dithiocarbamate) derivatives.

S.no	Complex	Reactants (gm)		Product (%) yield)	NaCl (gm) found (Calcd)	M.p.° (±1 °C)	M. wt. found (Calcd)	Analyses % found (Calcd)	
		Na salt of heterocyclic dithiocarbamate	Ph ₂ AsCl					As	S
1	Ph ₂ As (Pipdte)	(0.92)	(1.36)	80	0.29 (0.32)	153	389.60 (390.01)	18.99 (19.51)	16.25 (17.56)
2	Ph ₂ As(4-MePipdte)	(0.96)	(1.32)	78	0.28 (0.35)	158	408.40 (409.25)	18.34 (19.01)	15.70 (16.09)
3	Ph ₂ As (Morphdte)	(0.93)	(1.36)	76	0.29 (0.34)	157	396.37 (397.36)	18.90 (19.93)	16.17 (16.99)
4	Ph ₂ As(N-mePzdtc)	(0.96)	(1.31)	80	0.28 (0.34)	162	409.41 (410.08)	18.29 (19.51)	15.66 (16.70)
5	Ph ₂ As (Pzdtc)	(0.93)	(1.36)	75	0.29 (0.36)	140	395.36 (396.36)	18.94 (19.64)	16.21 (17.01)

Preparation of triphenylarsenic(V) bromo-(piperidine-dithiocarbamate) derivative

A freshly prepared sodium salt of pipdte (0.67 g, 3.65 mM) and Ph_3AsBr_2 (1.70 g, 3.64 mM) in benzene (~50 mL) were stirred for ~6 h at ~25 °C. The NaBr thus formed was filtered off and excess solvent was removed from the filtrate under reduced pressure to produce the compound as a yellow solid in quantitative yield. The product was recrystallized from benzene and n-hexane mixture.

Analysis showed As% (13.34), S% (11.73), C% (52.78), H% (4.63), N% (2.58) calculated for $\text{C}_{24}\text{H}_{25}\text{AsS}_2\text{NBr}$ As% (14.17), S% (12.15), C% (52.74), H% (4.60), N% (2.56). The other compounds were synthesized by similar methods. The synthetic and analytical data are summarized in table 9.

Preparation of triphenylarsenic(V) bis(piperidine-dithiocarbamate) derivative

Ph_3AsBr_2 (1.48 g, 3.17 mM) was mixed with freshly prepared sodium salts of pipdte (1.16 g, 6.32 mM) dissolved in benzene (~50 mL) and the reaction mixture was stirred for ~6 h at room temperature (~25 °C). The NaBr thus formed was filtered off and excess solvent removed from the filtrate under reduced pressure to produce the compound as a creamish colored solid in quantitative yield. The compound was recrystallized from benzene- n-hexane mixture (1 : 1).

The product on analysis showed As% (11.63), S% (20.45), C% (57.50), H% (5.65), N% (4.48) calculated for $\text{C}_{30}\text{H}_{35}\text{AsN}_2\text{S}_4$, As% (12.12), S% (21.47), C% (57.48), H% (5.62), N% (4.46).

The remaining compounds were also synthesized by similar methods. The synthetic and analytical data are summarized in table 9.

Table 9. Synthetic and analytical data of triphenylarsenic(V) bromo- and bis(heterocyclic dithiocarbamate) derivatives.

S.no	Complex	Reactants (gm)		Product (%) yield)	NaBr (gm) found (Calcd)	M.p. ^o (±1 °C)	M. wt. found (Calcd)	Analyses % found (Calcd)	
		Na salt of heterocyclic dithiocarbamate	Ph_3AsBr_2					As	S
1	$\text{Ph}_3(\text{Br})\text{As}(\text{Pipdte})$	(0.67)	(1.70)	78	0.37 (0.42)	153	546.43 (547.13)	13.34 (14.17)	11.73 (12.15)
2	$\text{Ph}_3(\text{Br})\text{As}(4\text{-MePipdte})$	(0.70)	(1.66)	73	0.36 (0.39)	158	560.83 (561.09)	13.01 (14.05)	11.43 (12.31)
3	$\text{Ph}_3(\text{Br})\text{As}(\text{Morphdte})$	(0.67)	(1.69)	76	0.37 (0.41)	157	548.40 (549.10)	13.30 (13.99)	11.69 (12.21)
4	$\text{Ph}_3(\text{Br})\text{As}(\text{N-mePzdtc})$	(0.70)	(1.66)	80	0.37 (0.42)	162	561.44 (562.23)	12.99 (13.51)	11.42 (11.90)
5	$\text{Ph}_3(\text{Br})\text{As}(\text{Pzdtc})$	(0.67)	(1.70)	75	0.65 (0.71)	140	547.71 (548.67)	13.31 (14.15)	11.70 (12.05)
6	$\text{Ph}_3\text{As}(\text{Pipdte})_2$	(1.16)	(1.48)	83	0.65 (0.69)	178	626.80 (627.20)	11.63 (12.12)	20.45 (21.17)
7	$\text{Ph}_3\text{As}(4\text{-MePipdte})_2$	(1.20)	(1.42)	80	0.62 (0.69)	143	654.82 (655.23)	11.13 (12.15)	19.58 (20.15)
8	$\text{Ph}_3\text{As}(\text{Morphdte})_2$	(1.17)	(1.47)	80	0.65 (0.71)	108	630.74 (631.57)	11.54 (12.70)	20.33 (21.09)
9	$\text{Ph}_3\text{As}(\text{N-mePzdtc})_2$	(1.12)	(1.45)	78	0.62 (0.67)	120	656.84 (656.91)	11.10 (12.05)	19.52 (20.17)
10	$\text{Ph}_3\text{As}(\text{Pzdtc})_2$	(1.09)	(1.51)	76	0.65 (0.68)	135	628.76 (629.25)	11.60 (12.09)	20.39 (21.50)

Acknowledgments

One of the authors (DKS) is grateful to UGC, Delhi for financial support and TheraChem Private Limited for FAB (ESI) Mass study.

References

- [1] S.S. Garje, V.K. Jain, E.R.T. Tiekink. *J. Organomet. Chem.*, **538**, 129 (1997).
- [2] J. Vrána, R. Jambor, A. Růžička, A. Lyčka, F. De Proft, L. Dostál. *J. Organomet. Chem.*, **723**, 10 (2013).
- [3] R. Bally. *Acta Crystallogr.*, **23**, 295 (1967).
- [4] R.K. Gupta, A.K. Rai, R.C. Mehrotra, V.K. Jain. *Polyhedron*, **3**, 721 (1984).
- [5] D. Coucouvanis. *Prog. Inorg. Chem.*, **11**, 233 (1970).
- [6] T.J. Patterson, M. Ngo, P.A. Aronov, T.V. Reznikova, R.H. Rice, P.G. Green. *Chem. Res. Toxicol.*, **16**, 1624 (2003).
- [7] H.P.S. Chauhan. *Coord. Chem. Rev.*, **173**, 1 (1998).
- [8] H.P.S. Chauhan, G. Srivastava, R.C. Mahrotra. *Polyhedron*, **3**, 1337 (1984).
- [9] H.P.S. Chauhan, B. Porwal, R.K. Singh. *Phosphorus, Sulfur Silicon Relat. Elem.*, **160**, 93 (2000).
- [10] S.S. Garje, V.K. Jain. *Coord. Chem. Rev.*, **35**, 236 (2003).
- [11] H.P.S. Chauhan, K. Kori, N.M. Shaik, U.P. Singh. *Phosphorus, Sulfur Silicon Relat. Elem.*, **180**, 31 (2005).
- [12] G.E. Manoussakis, C.A. Tsipis, A.G. Christophides. *Z. Anorg. Allg. Chem.*, **417**, 235 (1975).
- [13] C. Silvestru, I. Haiduc, E.R.T. Tiekink, D. de Vos, M. Biesemans, R. Willem, M. Gielen. *Appl. Organomet. Chem.*, **9**, 597 (1995).
- [14] B. Cvek, Z. Dvorak. *Curr. Pharm. Des.*, **13**, 1 (2007).
- [15] J. Sharma, Y.P. Singh, A.K. Rai. *Phosphorus, Sulfur Silicon Relat. Elem.*, **107**, 13 (1995).
- [16] P.K. Sharma, R.K. Sharma, A.K. Rai, Y.P. Singh. *Main Group Met. Chem.*, **27**, 51 (2004).
- [17] P.K. Sharma, H. Rehwani, A.K. Rai, R.S. Gupta, Y.P. Singh. *Bioinorg. Chem. Appl.*, **2006**, 1 (2006).
- [18] P.K. Sharma, H. Rehwani, R.S. Gupta, Y.P. Singh. *Appl. Organomet. Chem.*, **21**, 701 (2007).
- [19] Durgashanker, Y.P. Singh. *J. Coord. Chem.*, **62**, 1180 (2009).
- [20] R. Agrawal, J. Sharma, D. Nandini, A. Batra, Y.P. Singh. *J. Coord. Chem.*, **64**, 554 (2011).
- [21] D.K. Sharma, Y.P. Singh, J. Sharma. *Phosphorus, Sulfur Silicon Relat. Elem.*, **188**, 1194 (2013).
- [22] D.K. Sharma, Y.P. Singh, J. Sharma. *Main Group Chem.*, unpublished results (2013).
- [23] H.D. Yin, J. Zhai, Y.Y. Sun, D.Q. Wang. *Polyhedron*, **27**, 663 (2008).
- [24] G.E. Maciel, J.J. Nattsted. *J. Chem. Phys.*, **42**, 2427 (1965).
- [25] G.M. Bodner, L. Todd. *Inorg. Chem.*, **13**, 360 (1974).
- [26] B.W. Wenclawick, S. Uttich, H.J. Deiseroth, D. Schmitz. *Inorg. Chim. Acta*, **348**, 1 (2003).
- [27] R.L. Barker, E. Booth, W.E. Jones, A.F. Molidge, F.N. Woodward. *J. Chem. Soc. Ind.*, (London), **68**, 285 (1949).
- [28] A.D. Beveridge, G.S. Harris, F. Inglis. *J. Chem. Soc. A*, 520 (1966).
- [29] G. Marcotrigiano, G.C. Pellacani, C. Preti. *J. Inorg. Nucl. Chem.*, **36**, 3709 (1974).
- [30] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, 5th Edn, Longman, London (1979).