

Synthesis, characterization and structural comparisons of phosphonium and arsenic dithiocarbamates with alkyl and phenyl substituents



Courtney M. Donahue^a, Isabella K. Black^a, Samantha L. Pecnik^a, Thomas R. Savage^a, Brian L. Scott^b, Scott R. Daly^{a,*}

^aThe George Washington University, Department of Chemistry, 725 21st St., NW Washington, DC 20052, USA

^bLos Alamos National Laboratory, Los Alamos, NM 87545, USA

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ABSTRACT

The synthesis and characterization of the new arsenic dithiocarbamate complex $\text{As}[\text{S}_2\text{CNPh}_2]_3$ and three new phosphonium dithiocarbamates $[\text{PPh}_4][\text{S}_2\text{CNR}_2]$, where $\text{R}_2 = \text{Et}_2$, $(\text{CH}_2)_5$ and Ph_2 , are reported. $\text{As}[\text{S}_2\text{CNPh}_2]_3$ was prepared by treating AsI_3 with three equivalents of $\text{NaS}_2\text{CNPh}_2$ in a 2:1 mixture of H_2O and EtOH . The precipitate that formed was recrystallized from hot toluene to yield yellow prisms of $\text{As}[\text{S}_2\text{CNPh}_2]_3$ suitable for single-crystal X-ray diffraction (XRD). Attempts to prepare the known compound $\text{As}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$ using a similar route resulted in a mixture of $\text{As}[\text{S}_2\text{CN}(\text{CH}_2)_5]_3$ and the mixed iodide species $\text{As}[\text{S}_2\text{CN}(\text{CH}_2)_5]_2\text{I}$. Single-crystals of both compounds were isolated from concentrated $\text{Et}_2\text{O}/\text{CHCl}_3$ solutions and their structures are described here for the first time. $[\text{PPh}_4][\text{S}_2\text{CNR}_2]$ salts were prepared for comparison to arsenic dithiocarbamates by metathesis reactions with PPh_4Br and NaS_2CNR_2 in acetonitrile. All three salts could be obtained in high-purity from $\text{MeCN}/\text{Et}_2\text{O}$ solutions and crystal structures of $[\text{PPh}_4][\text{S}_2\text{CNEt}_2]$ and $[\text{PPh}_4][\text{S}_2\text{CN}(\text{CH}_2)_5]$ reveal charge-separated phosphonium cations and dithiocarbamate anions. The five new crystal structures are used to compare dithiocarbamate bond distances and angles in the presence and absence of arsenic. Nuclear magnetic resonance (NMR) spectra, infrared (IR) spectra, microanalyses, and melting points of the compounds are reported.

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1. Introduction

The chemistry of arsenic dithiocarbamates has been investigated since the first half of the 20th century [1–4]. While it is generally understood that dithiocarbamate ligands form robust complexes with arsenic and other “soft” p-block elements (as is often rationalized in terms of Pearson’s hard–soft acid–base theory) [5], it is less clear how varying the dithiocarbamate substituents affects As–S bonding and electronic structure. From a broad perspective, As–S bonding is of interest because of its role in arsenic toxicity mechanisms [6], and dithiocarbamate substituents appear to play a significant role in related arsenic binding and distribution in liquid–liquid extraction studies [7]. Our aim is to evaluate the role of dithiocarbamate substituents in $\text{As}[\text{S}_2\text{CNR}_2]_3$ electronic structure using S K-edge X-ray absorption spectroscopy (XAS), which requires a series of dithiocarbamate salts and arsenic complexes with high-purity and well-defined bond metrics. Here we describe the synthesis, characterization and structural

comparisons of several new phosphonium and arsenic dithiocarbamate complexes to be used in these efforts [8].

2. Results and discussion

2.1. Synthesis of $[\text{PPh}_4][\text{S}_2\text{CNR}_2]$ and $\text{As}[\text{S}_2\text{CNR}_2]_3$

In preparation for XAS studies, a systematically modified series of $\text{As}[\text{S}_2\text{CNR}_2]_3$ and $[\text{PPh}_4][\text{S}_2\text{CNR}_2]$ complexes were prepared (Scheme 1). These compounds were selected to determine how (1) the orientation of alkyl substituents and (2) the type of substituent (alkyl versus aryl) would affect dithiocarbamate bonding and electronic structure. As reported previously and shown below [9], the ethyl substituents in $\text{S}_2\text{CNEt}_2^-$ are typically found in a *trans* conformation while the alkyl-substituents in $\text{S}_2\text{CN}(\text{CH}_2)_5^-$ adopt a *cis* conformation that is enforced by the six-membered piperidyl heterocycle.

The salts $[\text{PPh}_4][\text{S}_2\text{CNR}_2]$, where $\text{R}_2 = \text{Et}_2$ (**1a**), $(\text{CH}_2)_5$ (**1b**), and Ph_2 (**1c**), were first prepared so that the bonding and structures of each anion could be evaluated in the absence of arsenic. The non-coordinating tetraphenylphosphonium cation (PPh_4^+) was

* Corresponding author. Tel.: +1 202 994 6934.

E-mail address: srdaly@gwu.edu (S.R. Daly).

	[PPh ₄][S ₂ CNR ₂]	As[S ₂ CNR ₂] ₃
R ₂ = Et ₂	1a	2a
R ₂ = (CH ₂) ₅	1b	2b
R ₂ = Ph ₂	1c	2c
	As[S ₂ CN(CH ₂) ₅] ₂ I 3	

Scheme 1. Numbering system used for phosphonium and arsenic dithiocarbamates.

chosen in preference to more traditional alkali metal cations in an effort to minimize intermolecular cation···sulfur interactions that could otherwise interfere with spectroscopic transitions associated with sulfur. In general, the synthesis of [PPh₄][S₂CNR₂] salts are relatively unexplored; only the structure of [PPh₄][S₂CNMe₂] has been reported from crystals obtained adventitiously from a failed reaction [10]. The salts **1a–1c** were prepared by metathesis reactions of NaS₂CNR₂ with PPh₄Br in acetonitrile (MeCN). After removal of the solvent and extraction with MeCN, analytically pure **1a–1c** could be obtained in high yield by vapor diffusion of diethyl ether (Et₂O) into the MeCN solutions. Large yellow prisms of **1a** and **1b** suitable for single-crystal X-ray diffraction (XRD) were collected and **1c** formed as a yellow microcrystalline solid.

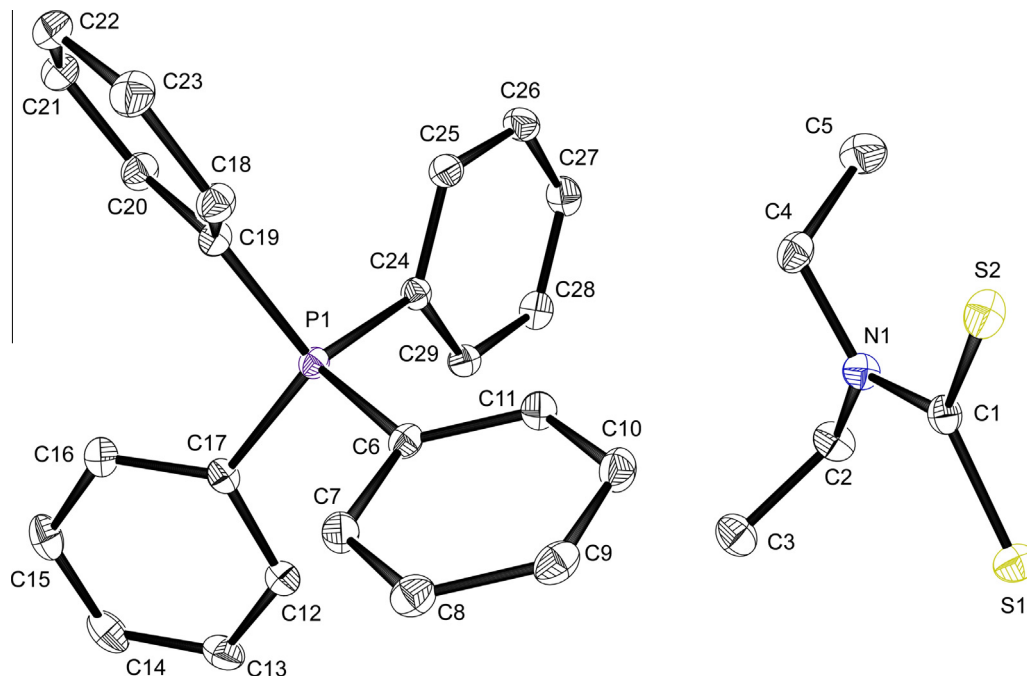


Fig. 1. Molecular structure of [PPh₄][S₂CNEt₂], **1a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted from the figure.

Table 1

Crystallographic data for [PPh₄][S₂CNEt₂] (**1a**), [PPh₄][S₂CN(CH₂)₅] (**1b**), As[S₂CN(CH₂)₅]₃ (**2b**), As[S₂CNPh₂]₃·C₇H₈ (**2c**·C₇H₈), and As[S₂CN(CH₂)₅]₂I (**3**).

	1a	1b	2b	2c ·C ₇ H ₈	3
Formula	C ₂₉ H ₃₀ NPS ₂	C ₃₀ H ₃₀ NPS ₂	C ₁₈ H ₃₀ N ₃ S ₆ As	C ₄₆ H ₃₈ N ₃ S ₆ As	C ₁₂ H ₂₀ N ₂ S ₄ IAs
FW (g mol ⁻¹)	487.63	499.64	555.73	849.97	522.36
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	P ₂ ₁ /c	P ₂ ₁ /c	P ₂ ₁ /c	P $\bar{1}$	P ₂ ₁ 2 ₁ 2 ₁
a (Å)	13.4423(18)	8.916(5)	17.2691(19)	10.437(4)	6.0207(7)
b (Å)	14.0324(18)	28.434(15)	11.8716(13)	13.306(4)	15.3440(18)
c (Å)	14.3843(19)	10.252(5)	12.1686(14)	16.024(5)	19.444(2)
α (°)	90.00	90.00	90.00	84.200(5)	90.00
β (°)	111.482(2)	99.040(6)	107.589(2)	89.661(5)	90.00
γ (°)	90.00	90.00	90.00	72.601(5)	90.00
V (Å ³)	2524.8(6)	2567(2)	2378.1(5)	2112.0(12)	1796.3(4)
Z	4	4	4	2	4
ρ _{calc} (g cm ⁻³)	1.283	1.293	1.552	1.337	1.932
μ (mm ⁻¹)	0.292	0.289	1.967	1.134	4.068
θ Range (°)	1.63/30.21	2.14/27.80	1.24/30.12	1.613/27.704	1.69/28.36
R(int)	0.0497	0.0443	0.0414	0.0564	0.0669
Data/restraints/parameters	7015/0/298	5952/0/307	6520/0/278	9589/95/505	4462/0/181
Goodness-of-fit (GOF) on F ²	1.038	1.024	1.072	0.985	0.914
R ₁ [I > 2σ(I)] ^a	0.0349	0.0350	0.0283	0.0434	0.0298
wR ₂ (all data) ^b	0.0940	0.0845	0.0611	0.1040	0.0527
Largest peak and hole (e Å ⁻³)	0.0452/−0.338	0.362/−0.282	0.405/−0.508	0.388/−0.378	0.523/−0.450
T (K)	293(2)	120(1)	293(2)	293(2)	293(2)

^a R₁ = ∑|F_o − |F_c|| / ∑|F_o| for reflections with F_o² > 2σ(F_o²).

^b wR₂ = [∑w(F_o² − F_c²)² / ∑(F_o²)²]^{1/2} for all reflections.

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