3746 *J. Am. Chem. Soc.* **1989**, *111*, 3746-3747

Preparation, Spectroscopic Characterization, and Crystal and Molecular Structure of 1,3,2-Benzothiazarsolium Tetrachloroaluminate: A Dicoordinate Arsenic Cation Containing As–S and As–N pπ-Bonding

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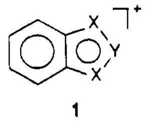
Recent studies of cationic dicoordinate phosphorus systems have unveiled a new dimension of phosphorus chemistry in terms of structure, bonding, and reactivity.[2] Perhaps most enlightening is the existence of pπ-bonding at the phosphorus center, without the protection of a steric shield. Analogous electronic environments for the heavier elements of group 15 (As, Sb, Bi) are extremely rare.[3]

The stabilizing features of the cationic, heteronaphthalenic framework **1** have allowed us to examine the interesting series **1a**, **1b**, and **1c**, which contain the first examples of npπ–3pπ (n = 3, 4, 5) bonding between the elements of group 15 (Y) and sulfur (X = S).[4,5] We now demonstrate further synthetic versatility for template **1** by the preparation and characterization of the 1,3,2-benzothiazarsolium cation **1e**, as a tetrachloroaluminate salt. Cation **1e** illustrates a unique example of S–As–N pπ bonding. In addition, this is the first structural characterization of a genuine[3b] cationic, dicoordinate arsenic center (arsenium).[3c]



1

a, X = S; Y = P
b, X = S; Y = As
c, X = S; Y = Sb
d, X = NMe; Y = P
e, X = NH, S; Y = As

2-Chloro-1,3,2-benzothiazarsole, **2**[6] (1.54 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred suspension of $AlCl_3$ (1.54 mmol) in CH_2Cl_2 (20 mL). The resulting red solution was stirred for 4 h, and slow removal of solvent resulted in the formation of air-sensitive, orange crystals (0.90 mmol, 58%, mp 125–128 °C), characterized[7] as 1,3,2-benzothiazarsolium (**1e**) tetrachloroaluminate.

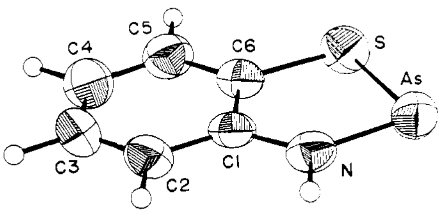


Figure 1. ORTEP view of cation **1e** with thermal ellipsoids set at 50% probability.

Table I. Selected Bond Lengths (Å) and Angles (deg) for the Cationic Unit **1e**

As–S	2.1536 (15)	C(1)–C(2)	1.397 (8)
As–N	1.776 (4)	C(2)–C(3)	1.356 (9)
N–C(1)	1.382 (7)	C(3)–C(4)	1.378 (10)
S–C(6)	1.736 (5)	C(4)–C(5)	1.380 (10)
C(1)–C(6)	1.383 (7)	C(5)–C(6)	1.394 (8)
N–As–S	89.27 (14)	N–C(1)–C(6)	115.8 (5)
As–N–C(1)	121.6 (3)	S–C(6)–C(1)	116.4 (4)
As–S–C(6)	96.95 (18)		

The ionic nature of **1e** in the solid state and in solution is evident from the IR and ^{27}Al NMR spectra, which are characteristic for the presence of $AlCl_4^-$ (485 cm^{-1}; 102 ppm).[2,5] Deshielding of the ^{1}H and ^{13}C NMR signals of **1e** with respect to **2** is typical for derivatives of **1**[4,5] and demonstrates effective delocalization of the molecular charge into the benzo moiety. The structural data[8] confirms the conclusions derived from the spectroscopy, revealing a planar cationic unit (**1e**) (Figure 1)[9] with a mean deviation of 0.020 Å and a maximum deviation from the plane of 0.050 (8) Å at C(4). Selected bond lengths and angles in the cation are presented in Table I. To our knowledge, the As–S (2.1536 (15) Å) bond is the shortest yet reported, other than those of arsenic(V) sulfides.[10] Likewise, the As(III)–N (1.776 (4) Å) bond is the shortest that we are aware of [cf. 1.832 (3) Å in $(CH_3)_2Si(tBuN)_2AsCl$, 1.843 (3) Å in $Fe_2(CO)_6[\mu$-tBuAs-(NSN)AstBu], 1.889 (6) Å in $Cr(CO)_5(Ph_2AsNSO)$].[11] The C–S (1.736 (5) Å) and C–N (1.382 (7) Å) bonds are also short and are identical with those found in analogues **1a**[4] and **1d**,[12] respectively. The discrete cationic and anionic units are bound together by an array of weak cation–anion contacts [shortest contacts: Cl---As 3.345 (1) Å and Cl---S 3.694 (2) Å]. Similar contacts are observed in polyatomic nonmetal salts[13] and

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(1) I. W. Killam Foundation Graduate Scholarship.

(2) See, for example: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367–382.

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(6) Reaction of *o*-aminothiophenol (0.08 mol) with $AsCl_3$ (0.08 mol) in the presence of NEt_3 (0.08 mol) in Et_2O produced 2-chloro-1,3,2-benzothiazarsole (0.009 mol), which was recrystallized from CH_2Cl_2. Elemental anal. Calcd: C, 30.85; H, 2.16; N, 6.00. Found: C, 30.63; H, 2.19; N, 5.91. IR (CsI plates, Nujol mull, cm^{-1}) 3290 (br, N–H), 740, 420, 230; NMR ($CDCl_3$) (ppm) ^{1}H (360 MHz), 7.53–6.99 (m), 6.63 (br, N–H); ^{13}C (91 MHz), 146.8, 126.3 (two resonances), 124.4, 121.4, 115.0.

(7) Elemental anal. Calcd: C, 19.64; H, 1.38; N, 3.82; S, 8.74. Found: C, 19.78; H, 1.24; N, 3.80; S, 8.87. IR (CsI plates, Nujol mull, cm^{-1}) 3230 (br, N–H), 760, 475 ($AlCl_4^-$). NMR (CD_2Cl_2) (ppm) ^{1}H (360 MHz), 8.40–7.60 (complex m), 8.39 (br, partial masking of aromatic signal); ^{13}C (91 MHz), 129.8, 127.8, 126.5, 118.9 (quaternary carbons not observed); ^{27}Al (94 MHz, wrt $Al(H_2O)_6^{3+}$), 102.7 ($\Delta\nu_{1/2}$ = 33 Hz, $AlCl_4^-$). Spectra obtained by the Atlantic Regional Magnetic Resonance Center, Halifax.

(8) Crystal data for $C_6H_5AsNSAlCl_4$: M = 366.89, monoclinic, $P2_1/c$, a = 6.4259 (5) Å, b = 23.654 (3) Å, c = 8.5859 (7) Å, β = 98.203 (6)°. V = 1291.68 (21) Å^3, Z = 4, D_c = 1.887 Mgm^{-3}, μ = 3.65 mm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.70930 Å) using $\theta/2\theta$ ($2\theta_{max}$ = 50°). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to residuals of R = 0.054, R_w = 0.042 for 1786 reflections with $I > 2.5\sigma(I)$ and with 128 variables. All computations were performed using the PC version of NRCVAX: Gabe, E. J.; Lee, F. L.; LePage, In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford: Clarendon, 1985; pp 167–174.

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other structurally characterized derivatives of **1**[4,12] and are believed to be nucleophilic charge transfer interactions.[13]

The novel[3] dicoordinate cationic environment for arsenic is stabilized by a number of factors,[4,14] including the delocalized, 10π-electron, naphthalenic framework, which necessitates the employment of As-S 4pπ-3pπ and As-N 4pπ-2pπ bonding. As such, compound **1e** represents the first structural evidence of As-S pπ-bonding and indicates energetic competition with As-N pπ-bonding.[15] Template **1** is now available for the generalization and diversification of pπ-pπ bonding between the heavier elements of the p-block and emphasizes the importance of isolobal[16] relationships in rationalizing nonmetal chemistry.

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Registry No. **1e**($AlCl_4$), 119998-84-4; **2**, 119998-85-5; $AlCl_3$, 7446-70-0; $AsCl_3$, 7784-34-1; *o*-aminothiophenol, 137-07-5.

Supplementary Material Available: Crystal structure experimental details, unit cell packing diagrams, and tables of atomic positional parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, and planes (10 pages); table of observed and calculated structure factors for $C_6H_5NSAs^+AlCl_4^-$ (17 pages). Ordering information is given on any current masthead page.

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Preparation and X-ray Crystal Structure of the First Pentacoordinate Silylsilicates[1]

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We wish to report herein the first synthesis and characterization of pentacoordinate silylsilicates in which a hitherto unknown type of a silicon-silicon σ bond is involved. Cleavage of the silicon-silicon bond of disilanes by nucleophiles like alkoxide and fluoride ions[2] has been well documented and often used as a method of preparing synthetically useful silyl anions. Pentacoordinate silylsilicates are implicitly postulated as key intermediates in these reactions. Very recently, Damrauer et al.[3] have reported detection of a silylsilicate by a gas-phase mass spectroscopic method, while Gordon et al.[4] have derived the pessimistic conclusion about the actual existence of such species from the ab initio MO calculation.

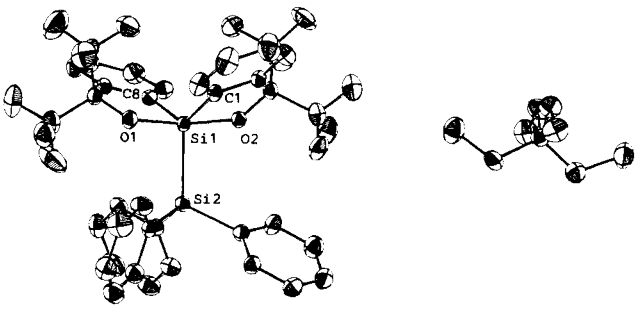
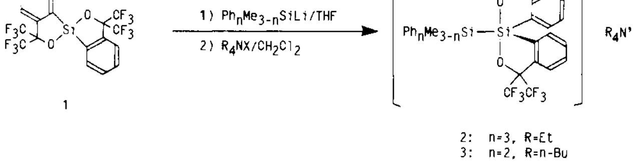


Figure 1. ORTEP drawing of pentacoordinate silylsilicate **2**. Selected bond distances (Å) and angles (deg) are as follows: Si1-Si2 = 2.403 (3), Si1-O1 = 1.831 (5), Si1-O2 = 1.838 (5), Si1-C1 = 1.903 (7), Si1-C8 = 1.899 (7); Si2-Si1-O1 = 94.3 (1), Si2-Si1-O2 = 93.6 (1), Si2-Si1-C1 = 114.1 (2), Si2-Si1-C8 = 118.8 (2), O1-Si1-O2 = 171.8 (2), O1-Si1-C1 = 93.2 (2), O1-Si1-C8 = 84.7 (2), O2-Si1-C1 = 84.6 (2), O2-Si1-C8 = 90.1 (2), C1-Si1-C8 = 126.9 (3).

Tetraethylammonium bis(α,α-bis(trifluoromethyl)benzenemethanolato(2-)C^2,*O*)(triphenylsilyl)silicate (**2**) and tetrabutylammonium bis(α,α-bis(trifluoromethyl)benzenemethanolato-(2-)C^2,*O*)(diphenylmethylsilyl)silicate (**3**) were prepared by the reaction of bis(α,α-bis(trifluoromethyl)benzenemethanolato-(2-)C^2,*O*)silane (**1**)[8] with 2 equiv of triphenylsilyl- or diphenylmethylsilyllithium in THF at room temperature, in 82% and 84% yields, respectively.[9]

On the other hand, (dimethylphenylsilyl)silicate could not be obtained by the reaction of **1** and (dimethylphenylsilyl)lithium under similar conditions. Substituents on the tetrahedral silicon atom could have a significant role on the stabilization of silylsilicates.



(1)

The structures of **2** and **3** were confirmed by means of NMR and negative-ion FAB MS.[9] The structure of **2** was further elucidated by X-ray analysis of the single crystals.[10] The ORTEP

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(9) Triphenylsilyllithium (3 mmol) in 5 mL of THF was added dropwise to **1** (1.5 mmol) in 3.2 mL of diethyl ether at 0 °C under argon. After 30 min kept at 0 °C, the mixture was stirred for 20 h at room temperature. The mixture was quenched with 2.5 mL of 6 M HCl at −60 °C and stirred for 30 min at room temperature. The solvent was removed, and tetraethylammonium bromide (1.875 mmol) in CH_2Cl_2 (25 mL) was added. After stirring for 30 min at room temperature, the mixture was extracted with water and dried over $MgSO_4$. Solvent removal gave yellow oil, which was crystallized from pentane-diethyl ether. The resulting solid was purified by recrystallization from THF-diethyl ether to give pure **2** in 82% yield. **2**: white crystals, mp 184-186 °C dec; ^1H NMR (acetone-d_6) δ 8.3-8.2 (m, 2), 7.7-6.9 (m, 21), 3.44 (q, J = 7.3 Hz, 8), 1.35 (tt, J = 7.3, 1.7 Hz, 12); ^{19}F NMR (acetone-d_6) δ −68.1 (q, J = 10.3 Hz), −69.2 (q, J = 10.3 Hz); negative-ion FAB MS m/e −771 (anion). Similar cation exchange of the crude lithium (diphenylmethylsilyl)silicate (1.5 mmol) with tetrabutylammonium bromide, followed by recrystallization from CH_2Cl_2-diethyl ether, gave white crystals of **3** in 84% yield. **3**: white crystals, mp 168-172 °C dec; ^1H NMR ($CDCl_3$) δ 8.4-8.0 (m, 2), 7.7-6.9 (m, 16), 2.8 (br t, J = 8 Hz, 8), 2.0-0.8 (m, 28), 0.37 (s, 3); ^{19}F NMR ($CDCl_3$) δ −73.4 (q, J = 9 Hz), −75.2 (q, J = 9 Hz); ^{29}Si NMR ($CDCl_3$) δ −21.8, −71.3; negative-ion FAB MS m/e −709 (anion).

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