Binary Group 15 Azides

Polyazide Chemistry: Preparation and Characterization of $As(N_3)_5$, $Sb(N_3)_5$, and $[P(C_6H_5)_4][Sb(N_3)_6]$**

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The binary arsenic and antimony azide species $As(N_3)_3$,[1–3] $[As(N_3)_4]^+$,[4] $[As(N_3)_4]^-$,[4] $[As(N_3)_6]^-$,[4,5] $Sb(N_3)_3$,[3,6] $[Sb(N_3)_4]^+$,[4] $[Sb(N_3)_4]^-$,[4] and $[Sb(N_3)_6]^-$[4] have been reported, and the crystal structures of $As(N_3)_3$,[3] $Sb(N_3)_3$,[3] and $[As(N_3)_6]^-$[4,5] determined.[7] In addition, the Lewis base stabilized species $M(N_3)_5{\cdot}LB$ (M = As, Sb; LB = pyridine, quinoline, NH_3, N_2H_4, NH_2CN) are known.[8] However, previous attempts[4] to obtain the neat pentaazides of arsenic and antimony were not successful. Even at low temperatures, attempted syntheses resulted in explosions that were described as "so intense that only pulverized glass remained".[4] Furthermore, $As(N_3)_5$ was predicted[4] to be a "highly unstable compound", based on its analogy to $AsCl_5$.[9] Herein, we communicate the synthesis and characterization of neat $As(N_3)_5$ and $Sb(N_3)_5$, and their conversion into the $[As(N_3)_6]^-$ and $[Sb(N_3)_6]^-$ ions, respectively. We also report the crystal structure of $[P(C_6H_5)_4][Sb(N_3)_6]$.

The reactions of AsF_5 or SbF_5 in SO_2 with excess $(CH_3)_3SiN_3$ result in facile and complete fluoride–azide exchange and yield clear yellow solutions of $As(N_3)_5$ or $Sb(N_3)_5$, respectively, [Eq. (1); M = As, Sb].

$$MF_5 + 5\,(CH_3)_3SiN_3 \xrightarrow{SO_2} M(N_3)_5 + 5\,(CH_3)_3SiF \qquad (1)$$

Removal of the volatile compounds (SO_2, $(CH_3)_3SiF$, and excess $(CH_3)_3SiN_3$) results in the isolation of the neat pentaazides.

As expected for highly endothermic, covalent polyazides, $As(N_3)_5$ and $Sb(N_3)_5$ are highly shock sensitive and can explode violently when touched with a metal spatula or by rapid change in temperature (e.g. freezing with liquid nitrogen). $As(N_3)_5$ was obtained as a yellow liquid. Its identity was established by the observed material balance, through ^{14}N NMR and vibrational spectroscopy, and its conversion with $[N_3]^-$ into the known[4,5] $[As(N_3)_6]^-$ ion. The observed low-temperature Raman spectrum of $As(N_3)_5$ is shown in Figure 1.

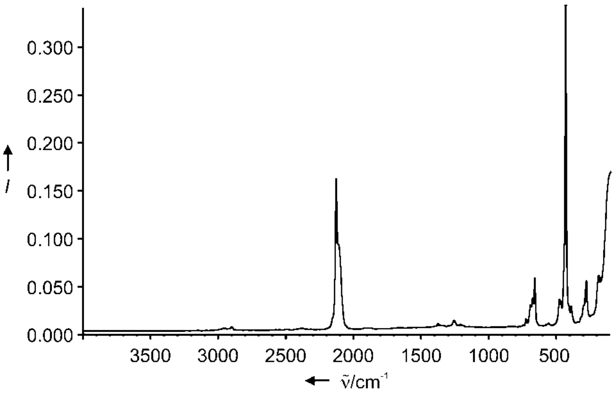

Figure 1. Low-temperature Raman spectrum of $As(N_3)_5$.

In contrast to a previous prediction,[4] neat arsenic pentaazide was found to be kinetically stable at ambient temperature, but highly explosive. The presence of covalent azido ligands[1–8,10–14] was confirmed by the observed ^{14}N NMR shifts of $\delta = -149$ ppm (N_β, $\Delta\nu_{1/2} = 42$ Hz), -160 ppm (N_γ, $\Delta\nu_{1/2} = 96$ Hz), and -282 ppm (N_α, extremely broad) in DMSO solution at 25 °C.

$Sb(N_3)_5$ was obtained as a pale yellow solid. It is even more sensitive than $As(N_3)_5$ and must be handled at reduced temperature. Warming the compound to ambient temperature results in violent decomposition and can cause serious damage. The identity of antimony pentaazide was established by the observed material balance, its Raman spectrum (Figure 2), and its reaction with $[N_3]^-$ to give the $[Sb(N_3)_6]^-$ ion. The calculated and observed vibrational frequencies and intensities for $As(N_3)_5$ and $Sb(N_3)_5$ are listed in Table 1. The agreement between the observed frequencies and those calculated for pentacoordinate trigonal-bipyramidal struc-

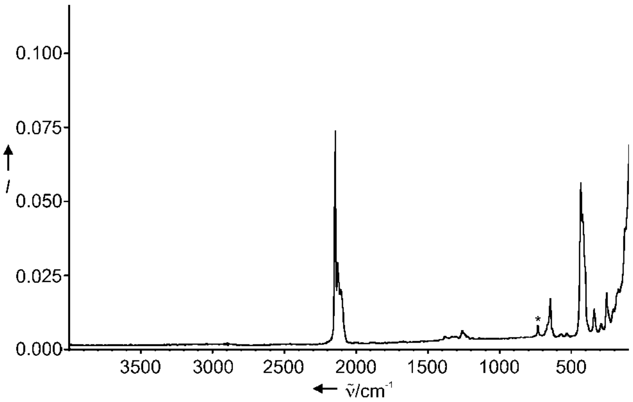

Figure 2. Low-temperature Raman spectrum of $Sb(N_3)_5$. The band marked by an asterisk is due to the Teflon-FEP sample tube.

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Table 1: Comparison of observed and calculated[a] vibrational frequencies [cm^{-1}] and intensities[b] for $As(N_3)_5$ and $Sb(N_3)_5$.

Band	Description	$As(N_3)_5$		$Sb(N_3)_5$	
		obsd Raman	calcd (IR) [Raman]	obsd Raman	calcd (IR) [Raman]
ν_1	$\nu_{as}N_3$	2162 [0.4]	2249 (366) [21]	2146 [10.0]	2198 (208) [35]
ν_2	$\nu_{as}N_3$	2135 [4.7]	2234 (775) [21]		2194 (936) [21]
ν_3	$\nu_{as}N_3$	2114 [2.6]	2210 (182) [35]	2127 [3.8]	2172 (282) [41]
ν_4	$\nu_{as}N_3$		2199 (417) [31]	2107 [2.6]	2166 (393) [25]
ν_5	$\nu_{as}N_3$		2191 (924) [24]	2097 [2.2]	2160 (941) [26]
ν_6	ν_sN_3	1262 [0.3]	1310 (48) [36]	1260 [0.7]	1262 (53) [32]
ν_7	ν_sN_3	1250 [0.3]	1305 (190) [8.8]	1249 [0.5]	1258 (151) [12]
ν_8	ν_sN_3		1284 (45) [21]	1239 [0.5]	1243 (17) [24]
ν_9	ν_sN_3		1283 (344) [3.1]	1221 [0.4]	1241 (290) [1.5]
ν_{10}	ν_sN_3		1276 (172) [9.3]		1238 (134) [7.9]
ν_{11}	δN_3	699 [0.8]	727 (91) [2.6]		661 (8) [1.5]
ν_{12}	δN_3	682 [1.0]	718 (16) [2.9]	667 [1.0]	658 (40) [3.9]
ν_{13}	δN_3		712 (29) [1.0]		653 (14) [1.9]
ν_{14}	δN_3		703 (59) [15]	646 [2.2]	647 (28) [15]
ν_{15}	δN_3	666 [1.7]	686 (9) [18]	630 [0.7]	634 (4) [28]
ν_{16}	δN_3		559 (9) [0.7]		540 (4) [1.3]
ν_{17}	δN_3		552 (3) [0.9]	532 [0.5]	529 (3) [0.9]
ν_{18}	δN_3		548 (5) [1.2]		525 (2) [1.2]
ν_{19}	δN_3		547 (4) [0.2]		524 (3) [1.3]
ν_{20}	δN_3		547 (12) [0.9]		522 (4) [1.1]
ν_{21}	$\nu_{as}MN$		514 (114) [3.1]	434 [7.5]	458 (74) [5.3]
ν_{22}	$\nu_{as}MN$		500 (100) [4.6]	421 [6.0]	452 (74) [5.8]
ν_{23}	$\nu_{as}MN$		488 (113) [4.6]		446 (69) [5.3]
ν_{24}	ν_sMN	437 [10.0]	463 (10) [49]	404 [3.8]	424 (4) [89]
ν_{25}	$\nu_{as}MN$	397 [0.8]	416 (6) [10]	382 [1.0]	400 (3) [14]
ν_{26}	δMN		333 (73) [0.7]		255 (62) [0.9]
ν_{27}	δMN		322 (47) [0.9]	291 [1.1]	250 (41) [1.6]
ν_{28}	δMN		314 (43) [2.6]	253 [2.5]	242 (11) [10]
ν_{29}	δMN	303 [0.8]	298 (6) [5.2]	239 [1.4]	234 (15) [5.2]
ν_{30}	δMN	284 [1.6]	291 (5) [9.4]	207 [1.6]	222 (29) [5.8]
ν_{31}	τ	194 [1.7]	183 (1) [4.2]	183 [2.3]	151 (2) [5.5]
ν_{32}	τ		173 (3) [1.5]	171 [2.6]	143 (4) [1.8]
ν_{33}	τ		167 (1) [4.4]		136 (1) [5.6]
ν_{34}	τ		148 (0.3) [0.7]		126 (1) [0.6]
ν_{35}	τ		112 (2) [3.2]		92 (2) [3.7]
ν_{36}	τ		95 (0) [8.5]		82 (1) [12]
ν_{37}	τ		92 (0.3) [9.5]		81 (0) [12]
ν_{38}	τ		83 (1) [4.4]		69 (1) [2.8]
ν_{39}	τ		53 (0) [4.6]		49 (0) [4.7]
ν_{40}	τ		45 (0) [6.3]		43 (0) [5.4]
ν_{41}	τ		43 (0) [7.7]		34 (0) [8.8]
ν_{42}	τ		31 (0) [4.5]		24 (0) [4.8]

[a] Our calculated MP2 minimum energy structures for $As(N_3)_5$ and $Sb(N_3)_5$ are derived from trigonal bipyramids and are very similar to those obtained at the B3LYP level.[4] [b] Observed Raman intensities are relative intensities; calculated IR intensities [km mol^{-1}] and calculated Raman [Å^4 amu^{-1}].

tures is good. However, it must be kept in mind that distinction between slightly different geometries based on the skeletal modes in these types of polyazido compounds is generally difficult, because the vibrational spectra are complex and not very sensitive to minor changes in the ligand arrangement.

The reactions of $As(N_3)_5$ and $Sb(N_3)_5$ with ionic azides, such as $[PPh_4]^+[N_3]^-$, produce the corresponding $[As(N_3)_6]^-$[4,5] and $[Sb(N_3)_6]^-$ salts, respectively, [Eq. (2); M = As, Sb].

$$M(N_3)_5 + [PPh_4]N_3 \xrightarrow{SO_2} [PPh_4][M(N_3)_6] \qquad (2)$$

Both tetraphenylphosphonium salts were isolated as colorless solids. The $[PPh_4][Sb(N_3)_6]$ salt can also be prepared from the corresponding $[SbCl_6]^-$ salt and $(CH_3)_3SiN_3$ in CH_3CN solution. However, the previously published[4] reaction conditions, that is, one single treatment at 25 °C for 24 h, were found insufficient. Even after seven prolonged treatments with large amounts of fresh $(CH_3)_3SiN_3$ only four of the original six chlorine ligands were replaced by azido groups, as shown by Raman spectroscopy and single-crystal X-ray diffraction studies. Heating to 82 °C in refluxing CH_3CN was required to achieve further chloride substitution.

Single crystals of $[PPh_4][Sb(N_3)_6]$ were obtained by recrystallization from CH_3CN solution. Because of the presence of a large counterion which serves as an inert spacer and suppresses detonation propagation, these salts are much less shock sensitive than neat $As(N_3)_5$ and $Sb(N_3)_5$, and are thermally surprisingly stable. Thus, a crystalline sample of $[PPh_4][Sb(N_3)_6]$ could be heated to its melting point at 104–106 °C without decomposition.

$[PPh_4][Sb(N_3)_6]$ crystallizes in the monoclinic space group *C2/c*. Its X-ray structure (Figure 3)[15] revealed the presence of $[PPh_4]^+$ and $[Sb(N_3)_6]^-$ ions without significant cation–anion interaction. The closest Sb···N and N···N contacts between neighboring anions are 5.0 Å and 3.2 Å, respectively. The structure of the $[Sb(N_3)_6]^-$ ion is only slightly distorted from perfect S_6 symmetry and is analogous to those of $[As(N_3)_6]^-$,[4,5] $[Si(N_3)_6]^{2-}$[16] $[Ge(N_3)_6]^{2-}$[17] and $[Ti(N_3)_6]^{2-}$,[18] and contrary to that of $[Te(N_3)_6]^{2-}$.[19] The structure of the $[Sb(N_3)_6]^-$ ion consists of an asymmetric SbN_9 unit with three azido groups covalently bonded in a trigonal pyramidal fashion to the antimony center. The remaining three coordination sites at the metal center are occupied by three symmetry related azido groups (symmetry operation $-x+3/2, -y+3/2, -z+1$). All three Sb–N bond of 2.064(2), 2.079(2), and 2.084(2) Å are significantly shorter than the 2.119(4) Å found for $Sb(N_3)_3$.[3]

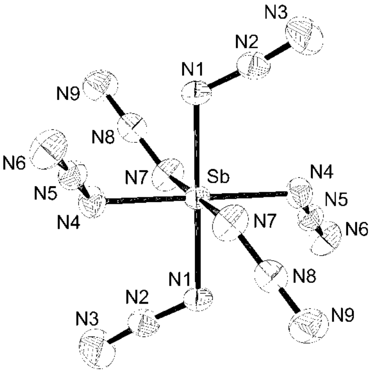

Figure 3. ORTEP drawing of the anionic part of the crystal structure of $[PPh_4][Sb(N_3)_6]$. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Sb-N1 2.065(2), Sb-N4 2.079(2), Sb-N7 2.085(3), N1-N2 1.220(3), N2-N3 1.120(3), N4-N5 1.222(4), N5-N6 1.127(4), N7-N8 1.222(3), N8-N9 1.128(4); N1-N2-N3 175.1(3), N4-N5-N6 175.1(3), N7-N8-N9 174.7(4), N1-Sb-N4 92.00(9), N1-Sb-N7 88.33(11), N4-Sb-N7 88.45(11), Sb-N1-N2 116.7(2), Sb-N4-N5 116.4(2), Sb-N7-N8 116.6(2).

Further support for the presence of the $[Sb(N_3)_6]^-$ ion is provided by the NMR spectrum. The ^{14}N NMR spectrum in DMSO shows resonances at $\delta = -141$ ppm (N_β, $\Delta\nu_{1/2} = 63$ Hz), -185 ppm (N_γ, $\Delta\nu_{1/2} = 103$ Hz), and -287 ppm (N_α, $\Delta\nu_{1/2} = 580$ Hz), that are characteristic for covalent azides.[1–8,10–14] Our spectrum differs, particularly in the N_γ region, significantly from that previously reported[4] (N_β: $\delta = -141$ ppm, $\Delta\nu_{1/2} = 45$ Hz; N_γ: $\delta = -154$ ppm, $\Delta\nu_{1/2} = 120$ Hz, $\delta = -163$ ppm, $\Delta\nu_{1/2} = 45$ Hz, $\delta = -173$ ppm, $\Delta\nu_{1/2} = 110$ Hz; N_α: $\delta = -244$ ppm, $\Delta\nu_{1/2} = 580$ Hz), for the $[N(C_2H_5)_4]^+$ salt in the same solvent and at the same temperature. We have observed similar shifts and multiple resonances for N_γ ($N_\alpha\delta = -245$ ppm; $N_\gamma\delta = -150$, -160, -168, and -169 ppm) in samples, prepared from $[SbCl_6]^-$, in which chlorine substitution was incomplete, as shown by Raman spectroscopy and their crystal structures. This result is in accord with our finding that, under the previously reported conditions,[4] the chloride/azide exchange is incomplete.

The observed Raman and IR spectra of $[P(C_6H_5)_4][Sb(N_3)_6]$ are shown in Figure 4, and the observed frequencies and intensities are listed in the Experimental Section. Assignments of the observed spectra were made by comparison with those calculated at the MP2/SBK+(d) level of theory and are given in the Experimental Section. The good agreement between the observed and calculated spectra confirms the results from the crystal-structure determination that, in its $[PPh_4]^+$ salt, the $[Sb(N_3)_6]^-$ ion closely approximates ideal S_6 symmetry.

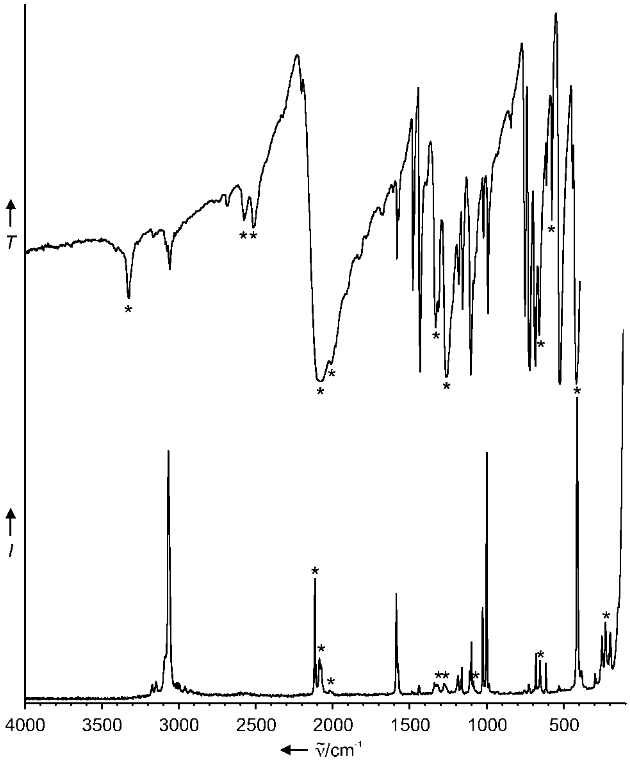

Figure 4. IR (top) and Raman (bottom) spectra of $[P(C_6H_5)_4][Sb(N_3)_6]$. The bands belonging to the $[Sb(N_3)_6]^-$ ion are marked with asterisks.

Experimental Section

Caution! *Arsenic and antimony azides are toxic, potentially hazardous, and can decompose explosively under various conditions! They should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs).*[3,18,19] *Teflon containers should be used, whenever possible, to avoid hazardous shrapnel formation. Rapid changes in temperature of* $As(N_3)_5$ *and* $Sb(N_3)_5$ *(whether pure or in* SO_2 *solution) can result in violent explosions. The manipulation of these materials is facilitated by handling them, whenever possible, in solution to avoid detonation propagation, the use of large inert counterions as spacers, and anion formation which increases the partial negative charges on the terminal* N_γ *atoms and thereby reduces the* N_β–N_γ *triple-bond character and the* *tendency for N_2 elimination.* ***Ignoring safety precautions can lead to serious injuries!***

All reactions were carried out in Teflon-FEP ampules (FEP = perfluoro ethylene propylene polymer) that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. All Teflon reaction vessels were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry argon atmosphere of a glove box.

Raman spectra were recorded at −80 °C in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm with power levels of 200 mW or less and a 180° geometry. Pyrex melting-point tubes that were baked out at 300 °C for 48 h at 10 mTorr vacuum or Teflon-FEP tubes with stainless steel valves that were passivated with ClF_3 were used as sample containers. IR spectra were recorded in the range 4000–400 cm^{-1} on a Midac, M Series, FT-IR spectrometer using KBr or AgCl pellets. The pellets were prepared inside the glove-box using an Econo press (Barnes Engineering Co.).

^{14}N NMR spectra were recorded unlocked at 36.13 MHz on a Bruker AMX 500 spectrometer using solutions of the compounds in DMSO in sealed standard glass tubes. Neat CH_3NO_2 ($\delta = 0.00$ ppm) was used as the external reference.

The starting materials AsF_5 (Ozark Mahoning) and $[P(C_6H_5)_4]I$ (Aldrich) were used without further purification. $(CH_3)_3SiN_3$ (Aldrich) was purified by fractional condensation and SbF_5 (Ozark Mahoning) by distillation prior to use. Solvents were dried by standard methods and freshly distilled before being used. $[P(C_6H_5)_4]N_3$ was prepared from $[P(C_6H_5)_4]I$ and AgN_3.

$As(N_3)_5$: $(CH_3)_3SiN_3$ (3.91 mmol) was condensed at −196 °C onto a frozen solution of AsF_5 (0.570 mmol) in SO_2 (1 mL). The reaction mixture was kept at −25 °C for 30 min and then slowly warmed to ambient temperature over a period of 4 h resulting in a yellow solution. Removal of all volatile material at ambient temperature in a dynamic vacuum resulted in the isolation of a colorless liquid (0.170 g, weight calculated for 0.570 mmol of $As(N_3)_5 = 0.162$ g). The obtained liquid was characterized by Raman and NMR spectroscopy.

$Sb(N_3)_5$: $(CH_3)_3SiN_3$ (4.84 mmol) was condensed at −196 °C onto a frozen solution of SbF_5 (0.609 mmol) in SO_2 (14 mmol). The reaction mixture was warmed to −25 °C and kept between −25 °C and −15 °C for 10 h resulting in a bright yellow solution. Removal of all volatile material at −15 °C in a dynamic vacuum resulted in the isolation of an intense yellow solid (0.216 g, weight calculated for 0.609 mmol of $Sb(N_3)_5 = 0.202$ g).

$[PPh_4][M(N_3)_6]$ (M = As, Sb): Neat PPh_4N_3 (0.43 mmol) was added to a cooled solution of $M(N_3)_5$ (0.43 mmol) in SO_2 (15 mmol) at −64 °C. The reaction mixture was kept at −25 °C and occasionally agitated. After 2 h, all volatiles were removed at ambient temperature in a dynamic vacuum, leaving behind solid $[PPh_4][M(N_3)_6]$. ($[PPh_4][As(N_3)_6]$: 0.285 g, weight calculated for 0.43 mmol = 0.288 g; $[PPh_4][Sb(N_3)_6]$: 0.313 g, weight calculated for 0.43 mmol = 0.307 g). Colorless single crystals of $[PPh_4][Sb(N_3)_6]$ were grown from a solution in CH_3CN by slow evaporation of the solvent in a dynamic vacuum. Raman spectrum of the $[As(N_3)_6]^-$ ion (50 mW, 20 °C): $\tilde{\nu} =$ 2125(4.9)/2085(3.0) ($\nu_{as}N_3$), 1331(0.6)/1269(1.0)/1251(0.6) (ν_sN_3), 666(1.5)/631(0.5) (δN_3), 418(10.0) (ν_sAsN), 379(1.1) ($\nu_{as}AsN$), 278(1.4) (δAsN), 165 (5.0) cm^{-1}. $[Sb(N_3)_6]^-$: IR (KBr): $\tilde{\nu} =$ 3329(mw)/2583(w)/2522(w) (combination bands), 2086(vs)/2016(s) ($\nu_{as}N_3$), 1337(m)/1318(m)/1264(s) (ν_sN_3), 663(m)/580(w) (δN_3), 424(s) cm^{-1} (νSbN). Raman (50 mW, 20 °C): $\tilde{\nu} =$ 2116(4.1)/2087 (1.4)/2075(1.1)/2018(0.3) ($\nu_{as}N_3$), 1319(0.5)/1275(0.5) (ν_sN_3), 653(1.4) (δN_3), 412(10.0) (ν_sSbN), 386(1.0) ($\nu_{as}SbN$), 229(2.5) (δSbN), 147 (3.0) cm^{-1}.

Optimizations of all structures were performed using second-order perturbation theory.[20,21] For the arsenic azides, the Binning and Curtis double-zeta valence basis set,[22] augmented with a d polarization function[23] was used for the arsenic and the 6-31G(d) basis set[24,25] for the nitrogen atoms. For the antimony azides, the Stevens, Basch, and Krauss (SBK) effective core potentials and the corresponding valence-only basis sets were used.[26] The SBK valence basis set for nitrogen was augmented with a d polarization function[25] and a diffuse s + p shell,[27] whereas only a d polarization function[28] was added to the antimony basis set. Hessians (energy second derivatives) were calculated for the final equilibrium structures to determine if they are minima (positive definite hessian) or transition states (one negative eigenvalue). All calculations were performed using the electronic structure code GAMESS.[29]

Unscaled calculated frequencies (cm^{-1}) and (infrared, km mol^{-1}) and [Raman, $Å^4 amu^{-1}$] intensities for the $[Sb(N_3)_6]^-$ ion (C_{2h} symmetry): A_g: 2219 (0) [82], 2200 (0) [48], 1273 (0) [77], 1267 (0) [41], 659 (0) [6.0], 645 (0) [23], 596 (0) [18], 409 (0) [121], 385 (0) [8.8], 236 (0) [5.2], 215 (0) [12], 128 (0) [9.3], 68 (0) [20], 30 (0) [17]; B_g: 2202 (0) [33], 1267 (0) [42], 652 (0) [0.9], 590 (0) [0.1], 549 (0) [0.4], 372 (0) [5.4], 225 (0) [4.6,] 128 (0) [8.4], 41 (0) [12], 24 (0) [9.9]; A_u: 2216 (1299) [0], 1268 (171) [0], 659 (5.8) [0], 590 (2.2) [0], 547 (5.8) [0], 424 (135) [0], 257 (122) [0], 195 (9.2) [0], 152 (1.0) [0], 68 (0.3) [0], 36 (1.1) [0], 19 (0.2) [0]; B_u: 2204 (1493) [0], 2193 (914) [0], 1271 (147) [0], 1268 (148) [0], 663 (25) [0], 650 (34) [0], 596 (7.0) [0], 429 (97) [0], 416 (112) [0], 247 (88) [0], 244 (52) [0], 166 (3.5) [0], 79 (4.1) [0], 71 (2.5) [0], 24 (0.5) [0].

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which 3130 ($R_{int} = 0.0545$) unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS: Madison, WI, 2001), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2001). Structure solution by direct methods (SHELXTL 5.10, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2, data to parameters ratio: 15.6:1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0356$, $wR2 = 0.0669$, $R1 = 0.0455$, $wR2 = 0.0684$ (all data), GOF on $F^2 = 0.900$. CCDC-240155 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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