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Preparation, characterization and *ab initio* computation of the first binary antimony azide, $Sb(N_3)_3$

Thomas M. Klapötke,* Axel Schulz and John McNamara

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

Reaction of SbI_3 with silver azide in acetonitrile solution gave $Sb(N_3)_3$ in high yield. The product was separated from silver iodide by extraction with acetonitrile. The identity of this first binary antimony azide was established by ^{14}N NMR and IR spectroscopy. The molecular structure of $Sb(N_3)_3$ was computed *ab initio* at the Hartree–Fock (HF) level of theory (HF/6-31 + G*) using a quasi-relativistic pseudo-potential (ECP) for antimony. The calculated and observed IR frequencies are in reasonable agreement.

We have recently been studying the reactions of various nitrogen, phosphorus and arsenic halides with silver azide and activated sodium azide.[1–4] In 1995 we reported on the synthesis of the first binary arsenic azide species $As(N_3)_3$ and $[As(N_3)_4]^+$.[4,5]

In contrast to the chemistry of halogen azides, which has been extensively explored in the last years,[1,6–9] studies on binary Group 15 azide compounds are still very limited. To our knowledge there are no reports on well established examples of covalently bound azides of the heavier Group 15 elements (Sb, Bi). Here we report on the reaction of SbI_3 with freshly prepared silver azide in MeCN which results in the formation of the binary antimony triazide $Sb(N_3)_3$ [equation (1)]. Pure

$$SbI_3 + 3\,AgN_3 \xrightarrow{\text{MeCN, r.t.}} 3\,AgI + Sb(N_3)_3 \qquad (1)$$

$Sb(N_3)_3$ was separated by extraction of the crude product with acetonitrile at room temperature, isolated as a white explosive solid and subsequently identified from its ^{14}N NMR and IR spectra.

Experimental

CAUTION: Pure $Sb(N_3)_3$ usually explodes on contact with a metal spatula or a metal syringe. The only product identified after an explosion was metallic antimony (and possibly nitrogen) but no antimony nitride.

Materials

Silver azide was always freshly prepared prior to use according to the previously published procedure and checked by IR spectroscopy.[6,10] Commercially available SbI_3 (Aldrich) was used without further purification. Solvents [MeCN and CH_2Cl_2 (Fisons)] were dried over P_4O_{10} and distilled prior to use. All manipulations were routinely performed under an inert-gas atmosphere (N_2, dry-box).

Spectroscopy

Infrared spectra were recorded at 20 °C as Nujol mulls between KBr plates on a Philips PU9800 FTIR spectrometer. The ^{14}N NMR spectra were recorded in 10 mm NMR tubes in CD_2Cl_2 solution (saturated solution) at 20 °C using a Bruker SY 200 spectrometer operating at 14.462 MHz. Good spectra could usually be obtained with a pulse width of 45 μs after 60 000 scans and are reported on the δ scale referred to external $MeNO_2$ in CD_2Cl_2 solution. Peak positions appearing downfield (high frequency) of the reference are reported as plus and those upfield (low frequency) of the reference as minus.

Table 1 Nitrogen-14 NMR data for $Sb(N_3)_3$, $As(N_3)_3$ and IN_3; chemical shifts in δ relative to $MeNO_2$ (linewidths Δν in Hz); connectivity $X–N_a–N_b–N_c$

	N_a	N_b	N_c	Ref.
$Sb(N_3)_3$	−324.1 (190)	−136.4 (30)	−172.8 (45)	This work
$As(N_3)_3$	−318.0 (150)	−131.1 (15)	−165.2 (30)	3
IN_3	−351.2 (350)	−121.9 (20)	−156.6 (65)	9

Preparation of $Sb(N_3)_3$

Silver azide (0.176 g, 1.17 mmol) was suspended in MeCN (10 cm^3) and treated with SbI_3 (0.171 g, 0.34 mmol) at 20 °C and the slurry stirred for 12 h. Filtration afforded a colourless solution. The remaining precipitate was then extracted with MeCN and the combined acetonitrile solutions evaporated to dryness leaving a white solid, which was washed twice with CH_2Cl_2 and dried in vacuum, $Sb(N_3)_3$ (0.058 g, 69%). For ^{14}N NMR data, see Table 1; IR, see Table 2. Despite several attempts we have so far been unable to grow crystals suitable for X-ray diffraction from MeCN or CH_2Cl_2 solutions (only microcrystalline powders were recovered after recrystallization). An attempt to sublime $Sb(N_3)_3$ resulted in an explosive decomposition of the material.

In two other experiments we treated SbI_3 with 1 or 2 equivalents of AgN_3, $Sb(N_3)_3$ and unreacted SbI_3 were the only identified products.

We also tried to prepare $Sb(N_3)_3$ from SbI_3 and activated sodium azide, NaN_3*, which is easier to handle and can be stored for some time, however no reaction was observed. This is probably due to the low solubility in MeCN of both NaN_3 and NaI while AgI is 'totally' insoluble in acetonitrile.

Computational methods

The structure and the vibrational spectrum of $Sb(N_3)_3$ were calculated *ab initio* at the Hartree–Fock (HF) level of theory with the program package GAUSSIAN 92/DFT.[11] For N a 6-31 + G* basis set was used, for Sb a quasi-relativistic pseudo-potential (ECP46MWB)[12] and the (5s5p)/[3s3p]-DZ basis set extended with a single set of d functions ($d_{exp} = 0.211$) was used.[13] These computations were carried out at TU, Berlin.

Results

The new binary antimony–nitrogen compound $Sb(N_3)_3$ was prepared according to equation (1) and identified unequivocally

Table 2 Infrared data (cm^{-1}) for $Sb(N_3)_3$, $As(N_3)_3$ and IN_3, and computed (HF) wavenumbers of $Sb(N_3)_3$[a]

		$Sb(N_3)_3$			
IN_3	$As(N_3)_3$	exptl.	HF[b]	HF, scaled[c]	Assignment
2055vs	2130m	2161m	2511m	2159	$\nu_{asym}(N_3)$
	2082vs	2095s	2485vs	2137	$\nu_{asym}(N_3)$
1170s	1238s	1260s	1405m	1208	$\nu_{sym}(N_3)$
		1205m	1376s	1183	$\nu_{sym}(N_3)$
648m		683w	727m	625	$\delta_{i.p.}(N_3)$
		668w			
		660m	725m	623	$\delta_{i.p.}(N_3)$
578m	561m	566w (br)	674m	580	$\delta_{o.o.p.}(N_3)$
		566w (br)	673m	579	$\delta_{o.o.p.}(N_3)$
360m	442m	420m	485m	417	$\nu(X–N_3)$
		400m	464s	399	$\nu(X–N_3)$
		n.o.	235m	202	δ(SbNNN)
Ref. 9	4	This work	This work	This work	

n.o. = Not observed. [a] Computed intensities (in km mol^{-1}) were calibrated as follows: $> 10^3$ = vs, $> 10^2$ = s, > 10 = m, > 1 = w. [b] Basis set and ECP, see Experimental Section. [c] Scaling factor 0.87.

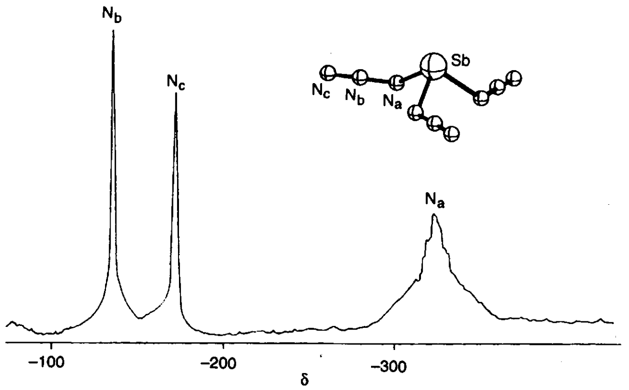

Fig. 1 The ^{14}N NMR spectrum of $Sb(N_3)_3$ (chemical shifts δ relative to $MeNO_2$)

on the basis of its IR and ^{14}N NMR spectra. For the covalently bound species three well resolved resonances have been found in the ^{14}N NMR spectrum (Fig. 1) and assignment of the individual resonances to N_a, N_b and N_c was made on the basis of the arguments given in early work by Witanowski[14] and three reports on ^{14}N NMR data for covalent azides given by us (connectivity: $X–N_a–N_b–N_c$).[2–4] The individual chemical shifts as well as linewidths found for $Sb(N_3)_3$ nicely compare to those of the structurally closely related $As(N_3)_3$ and also IN_3 (*cf.* electronegativities, Allred–Rochow: As, 1.8; As, 2.2; I, 2.2) (Table 1). Presumably as a result of the large quadrupole moment of ^{14}N, the spin–spin splitting which has been estimated to be less than 30 Hz was not observed (*cf.* linewidths, Table 1).[15]

The azide part of the IR spectrum was assigned by comparing the observed frequencies with those obtained for $As(N_3)_3$ and IN_3 (Table 2). Furthermore, to support the vibrational data of $Sb(N_3)_3$, the structure (Fig. 2) and vibrational frequencies were computed by *ab initio* methods. The structure was computed in C_3 symmetry and fully optimized at the HF level of theory [no imaginary frequencies, $E(\mathrm{HF}) = -495.09076E_h \approx -2.16 \times 10^{-15}$ J]. Table 2 shows the computed, scaled[16] and observed frequencies and their assignments.

Fig. 2 shows the HF-optimized structure of $Sb(N_3)_3$. As expected for a covalently bound azide, $Sb(N_3)_3$ displays a bent *trans* configuration with an N–N–N bond angle of 176°, and two significantly different N–N bond lengths. An interesting, though not unexpected,[17,18] structural feature of $Sb(N_3)_3$ undoubtedly is the N–Sb–N bond angle of 93° [*cf.* the valence angle at the central N in $(FSO_2)_2NN_3$ is 113°, and in the still hypothetical $N(N_3)_3$, 106.7°].[2,19,20]

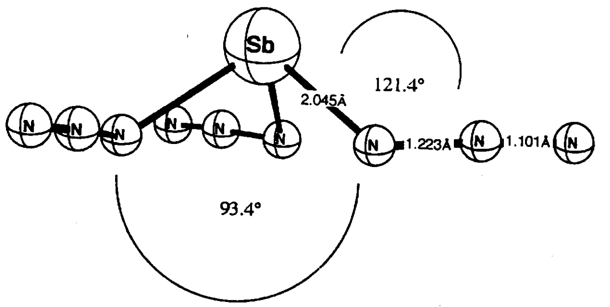

Fig. 2 The HF-optimized structure of $Sb(N_3)_3$. Dihedral angles N–N–N–Sb 179.1° and N–N–Sb–N 166.2°; N–N–N 176.1°

We are presently working on a comprehensive theoretical study of the bond situation in all $X(N_3)_3$ azides.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (KL 636/4–1 and 5–1) and the University of Glasgow for financial support. We are indebted to Jim Gall for recording the ^{14}N NMR spectra.

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Received 4*th March* 1996; *Paper* 6/01509C