Notiz / Note

A New Convenient One-Step Synthesis of $[(SCl)_2N]^+[SbCl_6]^-$ Containing the $[(SCl)_2N]^+$ Cation

Matthias Broschag, Axel Schulz, and Thomas M. Klapötke*

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin, Germany

Received May 27, 1994

Key Words: Sulfur-nitrogen chemistry / Sulfur-nitrogen-chlorine cation / Calculations, ab initio

The hexachloroantimonate salt of the $[(SCl)_2N]^+$ cation, $[(SCl)_2N]^+[SbCl_6]^-$ (**1**), was prepared in a one-step reaction from easily available $[SCl_3]^+[SbCl_6]^-$ and $N(SiMe_3)_3$ and isolated in good yield (60%). The compound was identified by chemical analyses and vibrational spectroscopy (IR, Raman). The geometrical and the vibrational data were also computed ab initio and are in good agreement with the experimental results.

The $[SNS]^+$ cation is probably the most important building block in sulfur-nitrogen chemistry[1]. The reactivity of this binary cation toward alkenes, alkynes, and nitriles is well documented[1,2]. Quite recently, Banister et al. published a general and easy route to $[SNS]^+$ salts starting from salts containing the $[(SCl)_2N]^+$ cation [Eq. (1)][2].

$$[(SCl)_2N]^+[AlCl_4]^- + SnCl_2 \rightarrow [SNS]^+[AlCl_4]^- + SnCl_4 \quad (1)$$

However, salts of the cation $[(SCl)_2N]^+$ are not commercially available. Usually $(SCl)_2N^+$ salts are prepared from $(NSCl)_3$ either by reaction with SCl_2 and a metal chloride (e.g. $AlCl_3$ or $SbCl_5$) [Eq. (2), (3)] or by reaction with $SCl_2/AgAsF_6$ [Eq. (4)][2,3,4].

$$(NSCl)_3 + 3\,SCl_2 + 3\,AlCl_3 \rightarrow 3\,[(SCl)_2N][AlCl_4] \quad (2)$$

$$(NSCl)_3 + 3\,SCl_2 + 3\,SbCl_5 \rightarrow 3\,\underset{\mathbf{1}}{[(SCl)_2N][SbCl_6]} \quad (3)$$

$$(NSCl)_3 + 3\,SCl_2 + 3\,AgAsF_6 \rightarrow 3\,AgCl + 3\,[(SCl)_2N][AsF_6] \quad (4)$$

Quite recently, Minkwitz et al. reported on a very interesting synthesis of $[(SCl)_2N][SbCl_6]$ from protonated hydrazoic acid and S_2Cl_2 [Eq. (5)][5].

$$[H_2N_3][SbCl_6] + 2\,S_2Cl_2 \rightarrow \mathbf{1} + 2\,HCl + N_2 + 2/8\,S_8 \quad (5)$$

Results and Discussion

The compound $[(SCl)_2N][SbCl_6]$ (**1**) was prepared from $[SCl_3][SbCl_6]$ and commercially readily available $N(SiMe_3)_3$ [Eq. (6)].

$$2\,[SCl_3][SbCl_6] + N(SiMe_3)_3 \xrightarrow{CCl_4} \underset{\mathbf{1}}{[(SCl)_2N][SbCl_6]} + 3\,Me_3SiCl + SbCl_5 + Cl_2 \quad (6)$$

Since **1** is the only product according to Eq. (6) that is not soluble in CCl_4 it can be separated by filtration. After digestion with CCl_4 the yellow material (**1**) was dried in dynamic vacuo and found to be analytically pure. The vibrational data of **1** are in good agreement with those previously reported[2] and compare also well with our ab initio computations (Table 1). Although ab initio calculations at the HF level usually predict too high frequencies due to the harmonic potential applied, the computed frequencies for the $[(SCl)_2N]^+$ cation (Table 1) compare very well with the experimental data and are just slightly too low.

Table 1. Computed (HF)[a] and experimentally observed vibrational frequencies for the $[(SCl)_2N]^+$ cation in $[(SCl)_2N][SbCl_6]$ (**1**)

HF[a]	IR[b]	Raman[c]	Assignment[d]
1088 (494)	1127 s	1128 (<1)	$\nu_{as}NS_2$
710 (49)	720 s	718 (2)	ν_sNS_2
599 (127)	662 m	654 (1)	δSNS
576 (76)	526 s	519 (2)	$\nu_{as}SCl$
492 (12)	508 m	503 (1)	ν_sSCl
413 (10)	447 m	453 (1)	δ_sClSN
225 (2)	360 s	n.o.	$\delta_{as}ClSN$
128 (0)	[e]	201 (3)	τ_{as}
105 (0.1)	[e]	126 (1)	τ_s

[a] HF/6-31+G* basis set; intensities refer to IR intensities. – [b] Powder between KBr plates, 25°C. – [c] 647.09 nm, 25 mW, 25°C. – [d] For assignment cf. also ref.[11]. – [e] Out of scale.

The structure of the $[(SCl)_2N]^+$ cation in $[(SCl)_2N][SbCl_6]$ was recently determined by X-ray diffraction[5]. As it is the case for most of the known $[(SCl)_2N]^+$ salts (e.g. $[SbCl_6]^-$ [5], $[BCl_4]^-$ [6], $[AlCl_4]^-$ [7], $[MoCl_5(NSCl)]^-$ [8]), the cation exhibits an u-shaped geometry (C_{2v}) in the solid state with an NSN angle of 150 ± 1°. The only known exception represents the salt $[(SCl)_2N][Re_2Cl_9]$[9] in which the SNS angle is compressed to 134°. In order to determine the most stable structure for the isolated cation we computed the $[(SCl)_2N]^+$ cation ab initio at the HF and correlated MP2 level of theory. The C_{2v} u isomer with an SNS angle close to 150° clearly turned out to be the most stable species (Table 2) which represents a true minimum according to the frequency analysis. The $[(SCl)_2N]^+$ cation with an SNS angle of 133.6° does not represent a minimum structure at the HF or MP2 level and lies 5.5 kcal mol^{-1} above the computed minimum structure (MP2, SNS 152.2°). Since the potential represented by a variation of the SNS angle in the

Chem. Ber. **1994**, *127*, 2187–2188 0009–2940/94/1111–2187 $ 10.00+.25/0

$[(SCl)_2N]^+$ cation is relatively flat (Figure 1) one can anticipate that the cation in $[(SCl)_2N][Re_2Cl_9]$ is forced to the more compressed structure by strong cation···anion interactions (cf. ref.[9]).

Table 2. Experimentally observed and ab initio computed structural parameters for the $[(SCl)_2N]^+$ cation (bond lengths in Å, angles in °, $E_{rel.}$ in kcal mol^{-1}). Corresponding anions: **1** $[SbCl_6]^-$, **2** $[AlCl_4]^-$, **3** $[MoCl_5(NSCl)]^-$, **4** $[Re_2Cl_9]^-$

	d(N−S)	*d*(S−Cl)	∡(SNS)	∡(ClSN)	E_{rel}
1	1.533(4)	1.911(7)	149.9(3)	110.4(2)	
2	1.528(2)	1.992(1)	151.0(2)	110.6(2)	
3	1.535(1)	1.988(7)	150.9(9)	110.0(5)	
4	1.615(11)	1.984(6)	133.6(17)	117.6(9)	
MP2 (FC)[a]	1.553	2.028	152.2	111.7	0.0
MP2 (FC)[a,b]	1.593	2.016	133.6	116.9	5.5

[a] HF/6-31+G* basis set. − [b] MP2 (FC) computation for a fixed SNS angle of 133.6°.

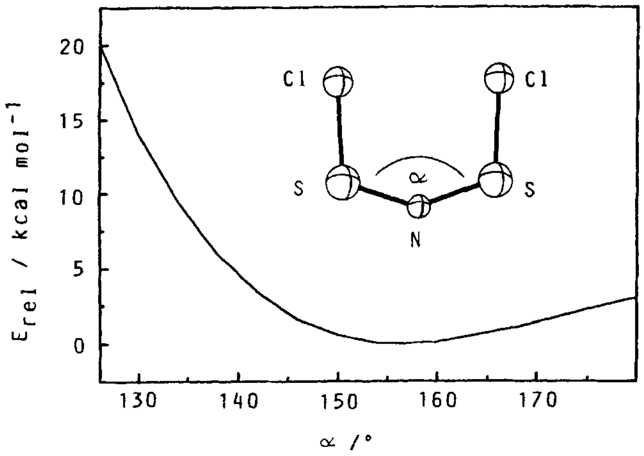

Figure 1. Energy potential curve of the SNS angle in the cation $[(SCl)_2N]^+$ (HF/6-31+G*)

Continuous financial support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

Synthesis of [SCl$_3$][SbCl$_6$]: Sulfur (1.00 g, 31.19 mmol) was suspended in 50 ml of CH_2Cl_2 and allowed to react at room temp. with a solution of $SbCl_5$ (9.32 g; 31.19 mmol) and chlorine (4.42 g; 62.37 mmol) in 50 ml of CH_2Cl_2. The reaction mixture was stirred for 12 h, the precipitated white solid was filtered off and three times washed with 20 ml of CH_2Cl_2. The product was dried in dynamic vacuo and obtained as analytically pure white solid in 82% yield (12.10 g). − IR: $\tilde{\nu}$ = 530 cm^{-1} m ($\nu_3SCl_3^+$), 518 m ($\nu_3SCl_3^+$), 360 sh ($\nu_3SbCl_6^-$).

Synthesis of [(SCl)$_2$N][SbCl$_6$] (**1**): $[SCl_3][SbCl_6]$ (3.00 g, 6.34 mmol) was suspended in 50 ml of CCl_4 and allowed to react at room temp. with a solution of $N(SiMe_3)_3$ (Aldrich, 0.741 g, 3.172 mmol) in 100 ml of CCl_4. The reaction mixture was stirred for 2 h, the precipitated yellow solid was filtered off and three times digested with 50 ml of CCl_4. The product was dried in dynamic vacuo and obtained as analytically pure yellow powder in 60% yield (0.92 g). − Cl_8NS_2Sb (483.5): calcd. N 2.90, S 13.26; found N 2.85, S 13.45. − IR and Raman: See Table 1; $[SbCl_6]^-$, Raman: $\tilde{\nu}$ = 332 cm^{-1} (10) (ν_1), 284 (2) (ν_2), 175 (9) (ν_5). − IR: $\tilde{\nu}$ = 351 cm^{-1} s (ν_3).

Computational Methods: The computations were carried out with the Gaussian 92 program using the 6-31+G* basis set[10].

---

[1] S. Parsons, J. Passmore, *Acc. Chem. Res.* **1994**, *27*, 101, and references therein.

[2] B. Ayres, A. J. Banister, P. D. Coates, M. I. Hansford, J. M. Rawson, C. E. F. Rickard, M. B. Hursthouse, K. M. Abul Malik, M. Motevalli, *J. Chem. Soc., Dalton Trans.* **1992**, 3097.

[3] G. G. Alange, A. J. Banister, P. J. Dainty, *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 175.

[4] A. J. Banister, A. G. Kendrick, *J. Chem. Soc., Dalton Trans.* **1987**, 1565.

[5] R. Minkwitz, U. Budde, B. Bäck, H. Preut, *Z. Naturforsch., Teil B*, **1993**, *48*, 243.

[6] O. Glemser, B. Krebs, J. Wegener, E. Kindler, *Angew. Chem.* **1969**, *81*, 568; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 598.

[7] O. Glemser, E. Kindler, B. Krebs, R. Mews, F. M. Schnepel, J. Wegener, *Z. Naturforsch., Teil B*, **1980**, *35*, 657.

[8] U. Müller, P. Klingelhöfer, U. Kynast, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1985**, *520*, 18.

[9] H. G. Hauck, P. Klingelhöfer, U. Müller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1984**, *510*, 180.

[10] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, K. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart, J. A. Pople, *Gaussian 92; Revision B*, Gaussian Inc., Pittsburgh, PA, **1992**.

[11] F.-M. Schnepel, *Spectrochim. Acta, Part A*, **1980**, *36*, 895.

[201/94]